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A.M. ZAVILOPULO,[1] S.S. DEMES,[2,3] E.YU. REMETA,[1] A.I. BULHAKOVA[1]

[1] Institute of Electron Physics, National Academy of Sciences of Ukraine
(21, Universytets'ka Str., Uzhgorod 88017, Ukraine; e-mail: gzavil@gmail.com)
[2] Institute for Nuclear Research (ATOMKI)
(4026 Debrecen, Hungary)
[3] Normandie University Le Havre, LOMC-UMR 6294 CNRS
(53, rue de Prony, BP 540, 76058 Le Havre, France)

ELECTRON-IMPACT IONIZATION OF THE GLUTAMIC ACID AND GLUTAMINE MOLECULES

The yield of positive ions formed as a result of the electron-impact dissociative ionization of glutamic acid (Glu-Acid) and glutamine (Gln) molecules in the gaseous phase has been studied both experimentally and theoretically. The experiment was performed using an MX-7304A monopole mass spectrometer in a mass number interval of 10–150 Da. The mass spectra of Glu-Acid and Gln molecules at various temperatures and the dynamics of the ionic fragment yield in an interval of initial substance evaporation temperatures of 310–430 K were studied, and the specific features of the relevant ionic fragment formation at the electron impact were analyzed in detail. Ab initio calculations of ionization potentials for glutamic acid and glutamine molecules were performed in the adiabatic approximation and on the basis of binding energies for the HOMO and LUMO orbitals of neutral molecules. The cross-sections of the single-electron ionization of both molecules by the electron impact were calculated in the framework of the binary encounter Bethe model and using the Gryziński formula. The calculated molecular constants were shown to agree well with the obtained experimental data.

K e y w o r d s: mass spectrum, amino acid, dissociative ionization, ionic fragment, ionization cross-section.

1. Introduction

Amino acids are known to be biologically important organic compounds. They are structural blocks of proteins containing the amine ($–NH_2$) and carboxyl (–COOH) groups. Most proteins consist of a combination of the nineteen so-called "primary" amino acids, i.e. they contain a primary amino group and a "secondary" amino acid of proline or imino acid (contains a secondary amino group), which are called standard or proteinogenic amino acids [1]. Amino acids were found in interstellar clouds and meteorites, which confirms one of the hypotheses about the extraterrestrial origin of the life on the Earth [2].

Glutamic acid is a neurotransmitter amino acid, being one of the important representatives of the class of "excitatory amino acids" [1, 3]. This acid, like glutamine itself, belongs to the group of non-essential amino acids and plays an important role in the life of biological organisms, in particular, in the strengthening of the immune system, which is extremely important for suppressing the viral pandemic [4, 5]. Glutamine, which penetrates the body through cell membranes, supports the protein synthesis, stabilizes fluid levels inside the cells, and supplies nitrogen for the synthesis of the purine ring and other vital

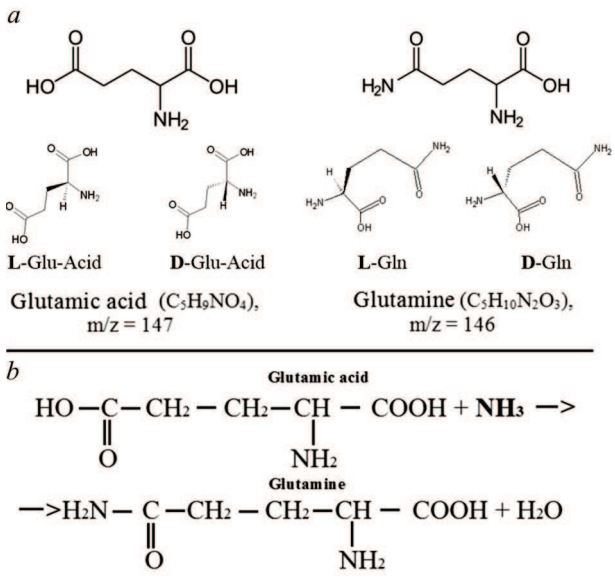


Fig. 1. Structural diagrams of glutamic acid and glutamine molecules (*a*) and the scheme describing the transformation of the glutamic acid molecule into the glutamine one (*b*)

compounds such as nucleotides, glucosamine, and asparagine.

The action of ionizing radiation on living organisms is known to stimulate the appearance of critical processes, namely, the degradation of living cells accompanied by irreversible changes and the emergence of carcinogenic modifications in living tissues. Most of those changes are invoked by low-energy (<100 eV) electrons, which destroy amino acids. As a result, fatal breaks of molecular bonds take place in living cells [3, 6]. That is why the interaction of low-energy electrons with complicated molecules (including amino acid ones) attracts a considerable interest from the viewpoint of monitoring the transformations in living cells under the action of ionizing radiation. Nevertheless, despite the large importance of studying the main mechanisms of structural changes in amino acid molecules under the action of low-energy electrons, the body of relevant data is quite scarce [3]. One of the most reliable methods for studying the structure of matter and the physical processes occurring in it is the mass spectrometry, because it allows obtaining useful information about the fragmentation of original molecules in the gas phase [7, 8].

The aim of this work was to experimentally study the process of electron-impact ionization of glutamic acid (Glu-Acid, $C_5H_9NO_4$) and glutamine (Gln, $C_5H_{10}N_2O_3$) molecules in the gas phase with the help of the mass spectrometric method at various evaporation temperatures of the initial substance and to measure the energy dependences describing the formation of positive ions of the parent glutamic acid and glutamine molecules owing to the electron impact. Another aim consisted in carrying out the theoretical calculations of the ionization potentials for those molecules, the binding energy of the HOMO and LUMO orbitals, and the cross-sections of the single-electron ionization in the framework of the binary encounter Bethe (BEB) model [9–11] and the Gryziński approximation [12] using the parameters of the molecular orbitals of those molecules calculated in the density functional theory (DFT) approximation and with the help of the Hartree–Fock (HF) method.

It is known that the properties of proteins are determined by the parameters of composing amino acids. In particular, the maximum negative charge in amino acids is localized at the oxygen atoms of the carboxyl group and at water molecules, whereas all hydrogen atoms are positively charged. In Fig. 1, *a*, the structural diagrams of glutamic acid and glutamine molecules, as well as their *L*- and *D*-forms, are shown. They clearly demonstrate the distinctive features of those molecules (although the difference between their molecular weights amounts to only 1 Da): in glutamine, the hydroxyl group of the acid residue of glutamic acid is substituted by the amino group. The process of such a substitution is illustrated in Fig. 1, *b* which exhibits the reaction of glutamic acid with ammonia; as a result, glutamine is formed.

Amino acid molecules exist in the form of various conformers. Furthermore, they have the *L*- and *D*-forms. Two types of amino acid isomerism are known. These are the structural isomerism, which is associated with the specific features in the structure of the carbon backbone and the relative arrangement of functional groups, and the optical (spatial) isomerism. Since α-amino acids contain a chiral carbon atom (*a*-atom), they can exist in the form of optical isomers (mirror antipodes), which play an important role in the protein biosynthesis process [1]. It is worth noting that a possible origin of the homochirality in biomolecules was studied in work [2] in detail.

The carboxyl group can rotate, whereas the hydrogen atom can be oriented both in the nitrogen direction and opposite to it. Besides that, the conformational variability of molecules favors the reorienta-

tion of flexible carboxyl (–COOH) and amine ($–NH_2$) groups and the formation of various intramolecular hydrogen bonds. For example, it can bind the unshared pair of nitrogen atoms with the hydrogen of the hydroxyl group (N...HO) or establish a bond between the hydrogen atom of the amine group and the oxygen atom of the carbonyl (NH...O=C) or hydroxyl (NH...OH) group (see Fig. 1, *a*).

The presence of a chiral carbon atom in the glutamine and glutamic acid molecules results in the existence of two enantiomeric forms [1]: *L* (*lævus*, left) and *D* (*dexter*, right) ones, with either of them being a specular image of the other (Fig. 1, *a*). This property of enantiomeric forms gives rise to the optical activity of molecules: when light passes through the vapor (the gas phase) of such molecules, its plane of polarization can rotate, if one of those forms dominates.

2. Experimental Technique

Earlier, we have performed mass spectrometric studies for a number of atomic and molecular objects [14, 15] including biomolecules [16, 17]. The experiment was carried out on an installation [15, 18], where a monopole mass spectrometer MX 7304A with the mass separation ΔM not worse than 1 Da was used as an analytical instrument. The molecular beam of examined molecules (Sigma-Aldrich, 99% purity grade) was formed making use of an effusion-type source fabricated from a stainless steel. The concentration of molecules in the region of intersection with the electron beam was within an interval of 10^{10}–10^{11} cm^{-3}. The ion source operated in the electric current stabilization mode and allowed electron beams with fixed energies from 5 to 70 eV, at currents of 0.05–0.5 mA, and with an energy scatter not worse than $\Delta E_{1/2} = 250$ MeV to be generated. The mass scale was calibrated on the basis of isotopic Ar, Kr, Xe, and N_2 peaks, and the electron energy scale on the basis of the initial intervals (5–15 eV) in the ionization cross-sections of a Kr atom and an N_2 molecule.

The experiment was performed in two stages. At the first stage, the mass spectra were studied at various temperatures. At the second stage, the energy dependences of the relative total cross-sections of the positive ion formation were measured within the energy interval of incident electrons from 5 to 60 eV. The required accuracy was provided by carrying out multiple measurements. The resulting error was not worse than 1.5% for the mass spectra, and at a level of 5–7% for the energy dependences. When measuring the temperature dependences, a special feedback device made it possible to maintain the temperature in the effusion source with an accuracy of ±0.05 K.

[1] The *D*/*L* nomenclature was introduced by G.E. Fischer to describe the relative configuration of monosaccharides [13]. Later it was extended onto amino acids.

3. Calculation of the Total Ground-State Energies for Glutamic Acid and Glutamine Molecules and Their Positive Ions

Despite the presence and development of some theoretical methods [19–21], the description of elementary processes with the participation of molecules still remains quite a difficult task. The main difficulty consists in the study of the interaction between low-energy electrons and molecular targets. In those processes, the incident electron modifies the molecule: it sequentially excites its rotational, vibrational, and electronic states. If the electron energy exceeds the ionization threshold, the electron impact leads to the direct or dissociative ionization. Such processes are very complicated, being often interrelated, which is confirmed by the non-triviality of their quantitative and qualitative theoretical descriptions.

The geometric and electronic structures of glutamic acid and glutamine molecules (Fig. 1, *a*), as well as their singly charged positive ions, were calculated using the GAUSSIAN program package [22]. The calculations were carried out in the framework of two approximations: the DFT and HF methods. The corresponding calculation procedure was described in works [15, 23, 24] in more details. The standard Gaussian Dunning basis set of the aug-cc-pVDZ type was applied in both calculation methods. In the DFT method, an exchange-correlation functional of the B3LYP type was used. The geometric structures of both isomers (*L*- and *D*-ones) for Glu-Acid and Gln molecules, as well as their positive ions, were optimized with the help of the quadratic approximation algorithm from the GAUSSIAN program package. When calculating the initial geometry of the molecules, the equilibrium interatomic distances were taken from the PubChem database [25–27].

The total energies of the considered molecules were determined for their ground states with singlet multi-

plicity and for their singly charged positive ions with doublet one. Since the ionization energy is defined as the difference between the corresponding total energies of the atom and its positive ion, the relative contribution of the molecular vibrational energy is insignificant. Therefore, to simplify the calculations, the vibrational energy of atoms in the molecules was neglected.

It is known that, under certain temperature conditions, molecules in the gas phase can be in various excited (*) and even ionized ($^+$) states [15]. The excitation energies are denoted as $E_{\rm el}$ for the electronic, $E_{\rm vib}$ for the vibrational, and $E_{\rm rot}$ for rotational states, with $E_{\rm el} \gg E_{\rm vib} > E_{\rm rot}$. The final products of reactions (dissociation, ionization, dissociative ionization) include atoms and molecular fragments, as well as their ions. They can exist not only in the ground and excited states, but can also form the bound states of negative ions [15]. The electronic excitation of a parent molecule decreases the electron detachment energy, whereas the excitation of the final ion increases this parameter. For instance, the process of direct ionization of an excited molecule giving rise to the appearance of the excited ion,

$$e^- + M(^*) \to M^+(^*) + 2e^-,$$

is characterized by the ionization potential

$$I(M(^*)) = I(M) \ - E(M(^*)) + E(M^+(^*)),$$

where $E(M(^*))$ is the excitation energy of the molecule, and $E(M^+(^*))$ the excitation energy of the ion. Thus, we have a set of ionization energy values, which is determined by the excitation energies $E(M(^*))$ and $E(M^+(^*))$ in the initial and final states, respectively. If $E(M(^*)) = E(M^+(^*)) = 0$, we obtain the ionization potential $I(M)$ from the ground state of a molecule into the ground state of its ion.

4. Discussion of Results

4.1. Mass spectra

In Fig. 2, the mass spectra of the glutamic acid and glutamine molecules in a mass interval of 10–150 Da, which were obtained at a molecular source temperature of 419 K and the electron energy $U_e = 70$ eV are shown. As one can see, those spectra are similar to each other: each of them includes 9 groups of lines, in which the lines are grouped near the line with the larger intensity. Those lines in the mass spectra of examined molecules correspond to fragments with different or the same masses, and they have almost the same intensity. Most of the observed mass peaks are typical of the fragmentation of the amino acid molecules [28], for which the dominant dissociation channel is associated with the loss of the neutral radical COOH. The common features of both (glutamic acid and glutamine) observed mass spectra are the presence of an intensive peak at $m/z = 84$; five substantially less intensive peaks at $m/z = 41$, 28, 56, 18, and 129; and two close-by-mass peaks at $m/z = 102$ (for Glu-Acid) and 101 (for Glu). A comparison of the relative peak intensities (see Table 1) demonstrates their large difference: the intensities of the peaks at $m/z = 16$ and 59 in the mass spectrum of glutamine are more than 40 times higher than their counterparts in the mass spectrum of glutamic acid. A substantial intensity difference is also observed for peaks at $m/z = 17$, 18, 44, 73, 83, and 101. On the other hand, the intensities of the peaks at $m/z = 74$ and 102 in the glutamic-acid mass spectrum are 2 and 11 times, respectively, higher than the corresponding peak intensities in the mass spectrum of glutamine.

The analysis of the obtained mass spectra allowed us to make a conclusion about the mechanisms governing the formation of the most intensive peaks of ionic fragments at the electron-impact dissociative ionization of the molecules. As was mentioned above, the ionization, i.e. the removal of an electron, leads to a weakening of the bonds in the molecular ion as compared to the neutral molecule. The most intensive peak of the ionic fragment with $m/z = 84$ can be formed owing to the loss of the COOH group, as well as hydrogen and oxygen atoms (see also the appearance energies and estimations in work [35]):

- glutamine,

$$\mathrm{C_5H_{10}N_2O_3} + e^- \to$$

$$\to \mathrm{C_4H_8N_2^+} + (\mathrm{COOH + OH}) + 2e^-, \quad (1a)$$

$$\to \mathrm{C_4H_7N_2^+} + (\mathrm{COOH + H_2O}) + 2e^-; \quad (1b)$$

- glutamic acid,

$$\mathrm{C_5H_9NO_4} + e^- \to$$

$$\to \mathrm{C_4H_6NO^+} + (\mathrm{COOH + H_2O}) + 2e^-, \quad (2a)$$

$$\to \mathrm{C_3H_2NO_2^+} + (\mathrm{COOH + 3H_2 + C}) + 2e^-. \quad (2b)$$

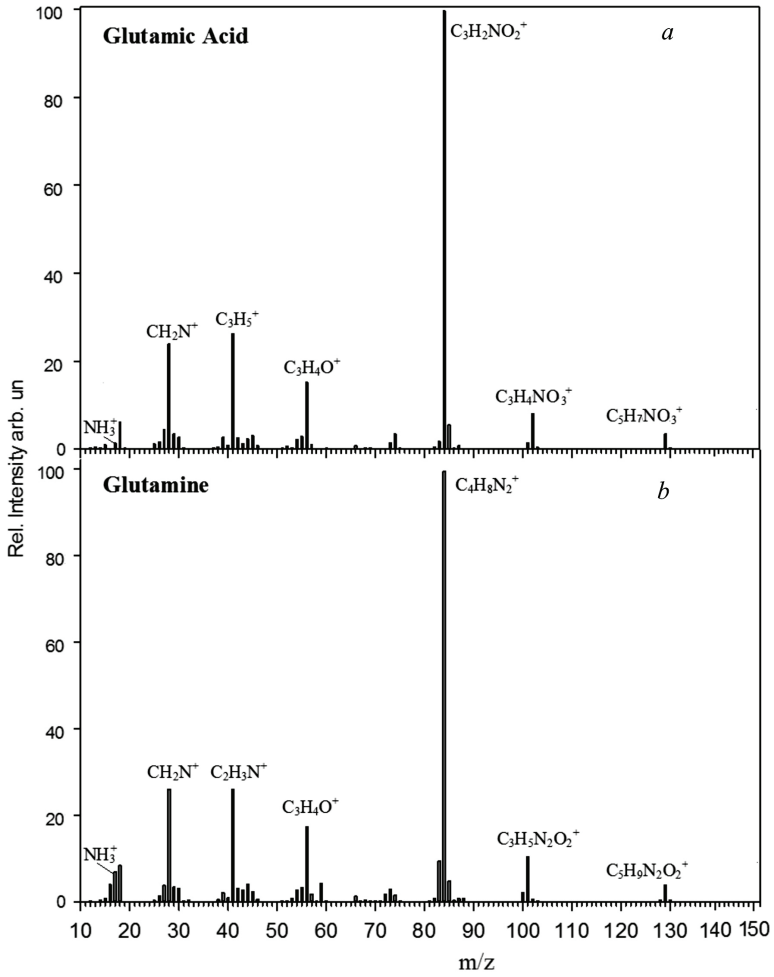


Fig. 2. Mass spectra of glutamic acid (a) and glutamine (b)

The other, less intensive, peaks in the mass spectra may correspond to the following molecular structures:

We would like to emphasize that the $C_3H_2NO_2$, C_4H_6NO, and $C_4H_8N_2$ fragments with $m/z = 84$ can contribute to the peak at $m/z = 85$, if one of their carbon atoms ^{12}C is substituted by its isotope ^{13}C. The amount of fragments with one ^{13}C isotope varied from about 1/25 to about 1/20 times the number of molecules with the ^{12}C isotopes.

Let us dwell in more details on the formation mechanism of some mass peaks.

i) $m/z = 28$. This mass peak can be associated with the isobaric ions CO^+ and CH_2N^+. However, the preference should be given to the latter, because the formation of just this HC–NH fragment dominates in the dissociation of amino acid molecules [3]:

• glutamine,

$$C_5H_{10}N_2O_3 + e^- \rightarrow$$
$$\rightarrow CH_2N^+ + COOH + NH_3 + C_3H_4O + 2e^-, \qquad (3)$$

• glutamic acid,

$$C_5H_9NO_4 + e^- \rightarrow$$
$$\rightarrow CH_2N^+ + (COOH + H_2O) + C_3H_4O + 2e^-. \qquad (4)$$

ii) $m/z = 41$. This mass peak may correspond to the isobaric ions $C_2H_3N^+$ and $C_3H_5^+$, which are the results of the following reactions:

• glutamine,

$$C_5H_{10}N_2O_3 + e^- \rightarrow$$
$$\rightarrow C_2H_3N^+ + COOH + C_2H_6NO + 2e^-, \qquad (5a)$$

$$\rightarrow C_3H_5^+ + COOH + CH_4N + NO + 2e^-; \quad (5b)$$

• glutamic acid,

$$C_5H_9NO_4 + e^- \rightarrow$$

$$\rightarrow C_2H_3N^+ + H_2O_3 + C_3H_4O + 2e^-, \quad (6a)$$

$$\rightarrow C_3H_5^+ + C_2H_3NO_2 + HO_2 + 2e^-; \quad (6b)$$

iii) $m/z = 56$. The $C_3H_4O^+$ fragment emerges due to the break of the bond between the carbon atoms in the molecular backbone chain (Fig. 1); namely:

• glutamine,

$$C_5H_{10}N_2O_3 + e^- \rightarrow C_3H_4O^+ + NH_3 + C_2H_3NO_2 + 2e; \quad (7)$$

• glutamic acid,

$$C_5H_9NO_4 + e^- \rightarrow C_3H_4O^+ + H_2O + C_2H_3NO_2 + 2e. \quad (8)$$

Note that the most intensive in the optical emission spectra of the studied molecules are the lines that correspond to molecular fragments of the carboxyl (–COOH) and amino ($–NH_2$) groups [29]. This fact means that the C–C, N–C, and C–O bonds have the lowest energy, which, in turn, leads to the appearance of ionic fragments of the carboxyl and amino groups in the mass spectra (Fig. 2). Really, the peak at $m/z = 101$ can appear, when the C_α–C_β bond becomes broken, which results in the formation of the molecular oxazolidinedione ion $C_3H_3NO_3^+$:

• glutamine,

$$C_5H_{10}N_2O_3 + e^- \rightarrow C_3H_3NO_3^+ + CH_4N + CH_3 + 2e^-, \quad (9)$$

• glutamic acid,

$$C_5H_9NO_4 + e^- \rightarrow C_3H_3NO_3^+ + C_2H_4 + H_2O + 2e^-. \quad (10)$$

Attention should be paid to the presence of the $(m/z = 129)$-peak in the mass spectra of glutamic acid and glutamine molecules with almost the same intensity (see Table 1). This fact allows us to assume that the ion of pyroglutamic acid $C_5H_7NO_3$ is formed under the action of low-energy electrons:

• glutamine,

$$C_5H_{10}N_2O_3 + e^- \rightarrow C_5H_7NO_3^+ + NH_3 + 2e^-, \quad (11)$$

• glutamic acid,

$$C_5H_9NO_4 + e^- \rightarrow C_5H_7NO_3^+ + H_2O + 2e^-. \quad (12)$$

In work [2], the mass spectrum of the fragments of the glutamic acid molecules observed at temperatures above 385 K was also explained as a result of the decomposition of its molecules with the formation of pyroglutamic acid ($C_5H_7NO_3$) and water molecules.

From the analysis of the electron reactions with the considered molecules, which were described above, a conclusion can be made that the detachment of the carboxyl group –COOH gives rise to the appearance of a number of intensive peaks at $m/z = 84$ (reactions (1) and (2)), as well as peaks at $m/z = 41$ (reaction (5)) and 28 (reactions (3) and (4)), which are five times less intensive. The detachment of the neutral fragment $C_2H_3NO_2$ results in the appearance of ionic fragments with $m/z = 41$ (in the case of a glutamic acid molecule) and 56 (for both molecules).

The more comprehensive analysis of processes (1)–(12) making use of theoretical calculations of the energies, lengths, and binding energies for parent and daughter ionic fragments, as well as neutral molecules, should be a result of the separate study [38–41] similar to that perfomed for the photoionization [8] and electron-impact ionization [35] processes.

In Table 1, the intensities of ionic fragments of the glutamine and glutamic acid molecules are compared with the data of works [30,31]. While analyzing those results, the conclusion can be drawn that the relative values obtained for the mass peak intensities obtained by us and in the cited works are in a rather good agreement. Note that the evaporation temperature of glutamine molecules was reported only in work [31].

4.2. Temperature dependences

The temperature of the gas of researched molecules is known [15, 16] to substantially affect the dissociative ionization process. In work [37], the thermal stability of amino acid molecules was considered. In work [33], the influence of the temperature on the vapor of glutamic acid molecules was analyzed, and the assumption was proposed about their decomposition into the pyroglutamic acid ($C_5H_7NO_3$) and water (H_2O) molecules at temperatures above 385 K.

In this work, the temperature dependences of the yield of positive ionic fragments of glutamic acid and glutamine molecules were measured. For the seven

Table 1. **Relative intensities of ionic fragments of glutamine and glutamic acid molecules**

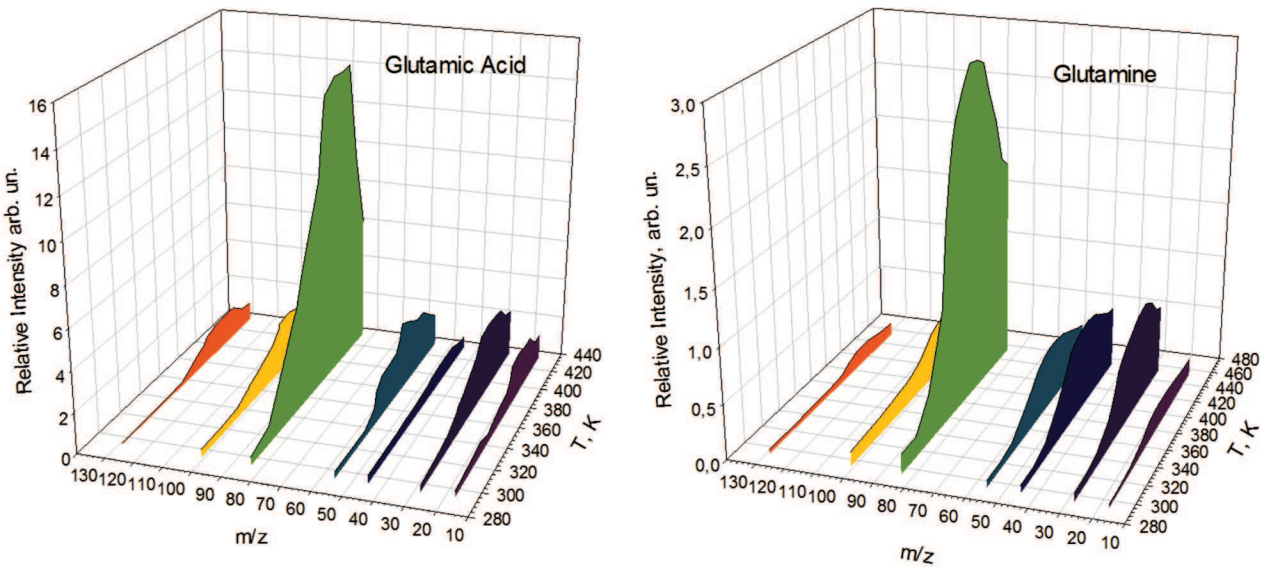
Ion	m/z, Da	Glutamine $C_5H_{10}N_2O_3$			Glutamic acid $C_5H_9NO_4$		
		Our data $T = 419$ K	NIST [30]	SDBS [31] $T = 430$ K	Our data $T = 380$ K	NIST [30]	SDBS [31] $T = 413$ K
NH_2^+	16	4.96	4.69	4.7	0.1	0.1	
NH_3^+ (OH^+)	17	6.96	6.69	6.7	1.38	1.3	1.8
CH_2N^+	28	25.99	26.09	26.1	24.5	24.7	26.7
CH_3N^+	29	2.82	3.39	3.4	3.4	3.49	3.5
CH_4N^+	30	2.48	3.7	3.4	2.6	2.7	2.7
$C_2H_3N^+$($C_3H_5^+$)	41	24.99	26.49	26.5	26.2	27.7	27.7
$C_2H_4N^+$	42	2.22	3.09	3.1	2.6	2.5	2.5
$C_3H_7^+$	43	1.95	2.59	2.6	1.15	1.2	3.4
$COOH^+$	45	3.85	4.19	4.2	3.2	3.1	3.0
$C_3H_4O^+$	55	2.79	3.49	3.5	2.9	2.8	2.8
$C_3H_4O^+$	56	17.86	18.69	18.7	15.2	15.3	15.3
$C_2H_5NO^+$	59	3.78	4.49	4.5	0.08	0.1	–
$C_2H_3NO_2^+$	73	2.78	2.99	3.0	1.35	1.4	1.4
$C_2H_4NO_2^+$	74	1.52	1.59	1.55	3.4	3.4	3.4
$C_3HNO_2^+$	83	8.91	9.69	9.7	1.67	1.7	1.7
$C_4H_8N_2^+$ ($C_3H_2NO_2^+$)	84	100	100	100	100	100	100
$C_3H_3NO_2^+$	85	4.49	4.99	5.0	5.55	5.6	5.6
$C_3H_3NO_3^+$	101	10.35	10.39	10.4	1.28	1.3	1.3
$C_3H_4NO_3^+$	102	0.6	0.7		8.06	8.1	8.1
$C_5H_7NO_3^+$	129	4.11	4.09	4.1	3.4	3.5	3.5

most intensive ionic fragments, the corresponding dependences are depicted in Fig. 3. As one can see, the temperature behavior of the analyzed quantity is similar for both molecules. Namely, in the initial section, the signal intensity increases, then it reaches saturation in a temperature interval of 370–410 K, and, afterward, a rather drastic decrease associated with the beginning of the decomposition of the molecules of examined substances, as well as their fragments, is observed. Such a behavior can be clearly seen for the $C_3H_2NO_2^+$ and $C_3H_4O^+$ fragments. Some features in the measured dependences attract attention. These are the changes of the curve slope at certain temperatures. Most likely, this effect is associated with processes (1)–(12) described above.

4.3. Energy dependences of the relative total cross-sections for the positive ion formation

The total current created at the collector by ions that were formed as a result of the interaction of the researched glutamic acid and glutamine molecules with electrons was measured at no potential difference between the deflecting electrodes in the mass spectrometer. By varying the electron energy in an interval of 5–60 eV, the energy dependence of the relative total cross-section for the positive ion formation was obtained. It should be noted that the measured cross-section corresponds to the direct ionization of parent molecules only in the subthreshold region, when the useful signal starts to grow. As the electron energy increases, the contributions of other processes into the cross-section magnitude become possible.

In Fig. 4, the energy dependences of the relative total ionization cross-sections for the parent molecules are shown. The measurements were performed with different increments of the incident electron energy: 0.2 eV in the threshold region (5–15 eV) and 1.0 eV in an interval of 16–60 eV. As one can see, the measured energy dependences are similar for both molecules. Their common features consist in a rather drastic cross-section growth in the interval from the



a *b*

Fig. 3. Temperature dependences of the formation of positive ions of the fragments of glutamic acid (*a*) and glutamine molecules (*b*). The electron energy is 70 eV

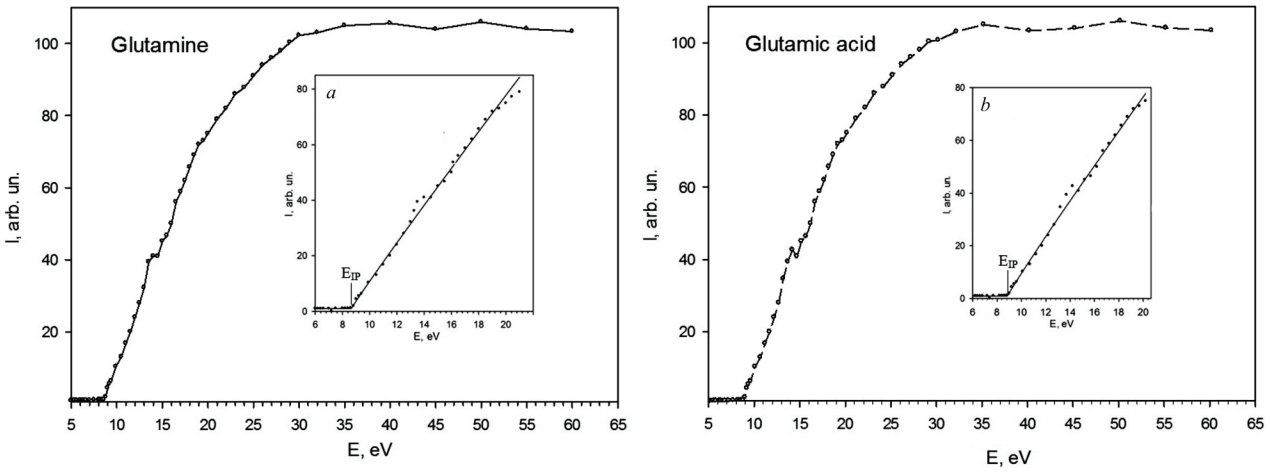


Fig. 4. Experimental dependences of the relative total ionization cross-sections of glutamine and glutamic acid molecules. The threshold sections of the corresponding dependences are shown in the insets. The solid curves are the results of fitting, and the symbols correspond to experimental data

threshold energy to about 20 eV and in the presence of small cusps at energies below 30 eV. In particular, those cusps are located at the following energies: at 14–14.5 and 19–19.5 eV for Gln, and at 14.2–14.7, 20.2–21.2, and 29.2–30.2 eV for Glu-Acid. In our opinion, they correspond to the appearance energies of molecular ionic fragments, which are formed at the dissociative ionization.

The flat-slope sections located above 30 eV also contain some peculiarities in the behavior of cross-sections. They are most likely associated with the opening of channels with higher ionization energies, e.g., the double-ionization channel. It should be noted that electron energies higher than 30 eV are potentially sufficient for the formation of doubly charged ions. We may assume that such doubly charged ions

Table 2. **Energy parameters of the *D*- and *L*-molecules of glutamine and glutamic acid**

D- and *L*-glutamine (Gln $C_5H_{10}N_2O_3$)			*D*- and *L*-glutamic acid (Glu-Acid $C_5H_9NO_4$)		
Energy	*D*-Gln	*L*-Gln	Energy	*D*-Glu-Acid	*L*-Glu-Acid
Adiabatic approximation (DFT)					
$E_t[M]$, a.u.	−531.848802	−531.846718	$E_t[M]$, a.u.	−551.723672	−551.71741
$E_t[M+]$, a.u.	−531.534418	−531.532443	$E_t[M+]$, a.u.	−551.397838	−551.393955
$I(M)$, eV	8.555	8.552	$I(M)$, eV	8.866	8.802
Adiabatic approximation (HF)					
$E_t[M]$, a.u.	−528.778722	−528.776096	$E_t[M]$, a.u.	−548.618111	−548.611595
$E_t[M^+]$, a.u.	−528.522005	−528.526725	$E_t[M^+]$, a.u.	−548.323649	−548.319627
$I(M)$, eV	6.986	6.786	$I(M)$, eV	8.013	7.945
Molecular-orbital approximation (DFT)					
$E_b^{\mathrm{HOMO}}(M)$, a.u.	−0.257323	−0.256457	$E_b^{\mathrm{HOMO}}(M)$, a.u.	−0.269497	−0.26808
$I(M)$, eV	7.002	6.979	$I(M)$, eV	7.333	7.295
Molecular-orbital approximation (HF)					
$E_b^{\mathrm{HOMO}}(M)$, a.u.	−0.401417	−0.399521	$E_b^{\mathrm{HOMO}}(M)$, a.u.	−0.413427	−0.412692
$I(M)$, eV	10.923	10.872	$I(M)$, eV	11.250	11.230
Experimental values of ionization potential, eV					
Gln			Glu-Acid		
8.64 ± 0.25			8.86 ± 0.25		

of the studied amino acid molecules are unstable and decay, but the confirmation of this hypothesis requires special experiments. Note also that the electron energies above 30 eV also exceed the energies of many molecular orbitals in the molecules concerned.

The ionization energies of glutamine and glutamic acid molecules were determined by analyzing the threshold sections of the curves making use of the fitting procedure according to the Levenberg–Marquardt algorithm [15, 32]. The fitting expression

$$u + a\,(E - ip)^d$$

with the parameters u, a, p, and d was applied. The Gaussian distribution was also used to account for the energy spread of electrons ΔE (see work [16]).

The threshold sections of the energy dependences are shown in insets (a) and (b) of Fig. 4 for glutamine and glutamine acid molecules, respectively. As one can see, the experimental curves and the fitting results correlate well with one another, which made it possible to determine the ionization energies (potentials) for the parent molecules: $E_{IP} = 8.64 \pm 0.25$ eV for Gln and $E_{IP} = 8.86 \pm 0.25$ eV for Glu-Acid (see Table 2). It should be noted that the presented values turned out slightly lower–by 0.16 and 0.04 eV, respectively–than the values reported by us earlier in work [33]. This discrepancy appeared, because the refined values were obtained with the help of additional experimental data and making the fitting procedure better.

4.4. Calculation of ionization potentials for glutamine and glutamic acid molecules

The ionization potentials of the researched molecules were calculated in the framework of the *ab initio* approach using the DFT and HF methods, as was described in Section 2. Two separate approximations were applied at that. In the first adiabatic, approximation, the difference between the total ground-state energies of the parent ion, $E_t[M^+]$, and the neutral molecule, $E_t[M]$: $I(M) = E_t[M^+] - E_t[M]$, was used. In this case, the states of the molecules and

their ions correspond to the calculated equilibrium interatomic distances.

In the second approximation, which is simpler, the ionization potential of the molecule can be determined by calculating its molecular orbitals. In this approximation, the so-called lowest unoccupied (LUMO) and highest occupied (HOMO) molecular orbitals of the molecule are determined. According to Koopmans' theorem, the binding energies E_b of those orbitals allow the ionization energy (potential) of the molecule and the electron affinity energy of the molecule, E_a, to be determined. In particular, the binding energy of an electron equals $I(M) = -E_b^{\mathrm{HOMO}}(M)$ in the HOMO and $E_a = -E_b^{\mathrm{LUMO}}(M)$ in the LUMO.

Table 2 contains the total energy values calculated for two isomers (L- and D-) of the neutral glutamine and glutamic acid molecules and their singly charged positive ions, as well as the adiabatic ionization potentials calculated for them using the DFT and HF models. The table also contains the binding energies of the HOMOs and LUMOs of those neutral molecules, for which the ionization potential values were calculated with the help of the indicated methods. Calculations using the DFT method in the adiabatic approximation gave the values $E_b = 8.555$ eV for D-Gln, 8.552 eV for L-Gln, 8.866 eV for D-Glu-Acid, and 8.802 eV for L-Glu-Acid. From Table 2, one can see that the theoretical values are lower by about 0.08–0.09 eV for the glutamine molecule and by about 0.06 eV for the glutamic acid molecule than the corresponding experimental data. The ionization potentials obtained using the HF method in the adiabatic approximation are lower than the values obtained using the DFT method. At the same time, the values obtained in the molecular-orbital approximation turned out larger.

The results of calculations quoted in Table 2 demonstrate that the values obtained for the ionization potentials in the more accurate adiabatic approximation are always slightly larger than the values obtained in the molecular-orbital approximation. The corresponding excess in the DFT case equals 1.553 eV for D-Gln, 1.573 eV for L-Gln, 1.533 eV for D-Glu-Acid, and 1.507 eV for L-Glu-Acid. The ionization potentials of the glutamine and glutamic acid D-molecules are larger than the ionization potentials of the corresponding L-molecules. The same situation takes place in the case of HOMO/LUMO calculations as well.

The values of the ionization potential calculated for the L- and D-isomers of both examined molecules slightly depend on their shape (see Fig. 1). For instance, the corresponding difference is 0.003 eV between the results obtained for the D- and L-molecules of glutamine in the DFT approximation (0.023 eV for HOMO/LUMO calculations). In the case of the glutamic acid D- and L-molecules, this difference is some larger: 0.064 eV for the DFT approximation and 0.038 eV for HOMO/LUMO calculations. The ionization potential of the glutamine D-molecule is by 0.311 eV lower than the corresponding value for the glutamic acid D-molecule (by 0.331 eV according to HOMO/LUMO calculations). In the case of the glutamine and glutamic acid L-molecules, this difference amounts to 0.250 eV (0.316 eV according to HOMO/LUMO calculations).

Note that the energy structure of some amino acids, including the glutamine and glutamic acid L-molecules, was theoretically studied in work [34]. The calculation technique was similar to that applied by us. The adiabatic values obtained for the ionization potential in the case where the parent molecule and its ion are in the equilibrium state are 8.52 eV for Gln and 8.93 eV for Glu-Acid. One can see that the indicated values are in good agreement with the results of our calculations and with the experimental data.

4.5. Calculation of total single-ionization cross-sections of glutamine and glutamic acid molecules

As was indicated above, we used the BEB model [9–11] and the classical Gryziński approximation [12] in order to estimate the single-ionization cross-sections of studied molecules. In the framework of the BEB model, the expression for the cross-section of electron ionization from a molecular orbital looks like

$$\sigma_i(t) = \frac{S}{t+u+1}\left\{\frac{Q}{2}\left(1-\frac{1}{t^2}\right)\ln t + \right.$$

$$\left. + (2-Q)\left[\left(1-\frac{1}{t}\right) - \frac{\ln t}{t+1}\right]\right\}, \qquad (13)$$

where $t = T/B$, T is the kinetic energy of an incident electron; B is the binding energy of the removed electron in the molecular orbital, $u = U/B$, U is the average kinetic energy of electrons in the molecular

Table 3. **Fitting parameter values for various fitting formulas of the total ionization cross-sections of the D-forms of Glu and Glu-Acid molecules normalized by the result of BEB-DFT calculations**

Fitting parameter		Fitting formula		
		Binary-Encounter-Dipole (BED) (15)	Binary-Encounter-Bethe (BEB) (16)	Gryziński (17)
a	Gln	113.67 ± 17.07	28.91 ± 4.06	0.543 ± 0.051
	Glu-Acid	222.83 ± 26.96	56.08 ± 6.48	0.498 ± 0.069
b	Gln	242.12 ± 65.68	535.24 ± 20.59	105.86 ± 5.55
	Glu-Acid	80.16 ± 102.87	657.32 ± 31.99	146.69 ± 10.78
c	Gln	-670.26 ± 91.85	-028.9 ± 36.4	1.136 ± 0.017
	Glu-Acid	-566.41 ± 143.14	-1273.8 ± 56.1	1.094 ± 0.017
d	Gln	–	–	1.568 ± 0.060
	Glu-Acid	–	–	1.529 ± 0.083

orbital that becomes ionized,

$$S = 4\pi a_0^2 N \left(\frac{R}{B}\right)^2, \quad Q = \frac{2BM_i^2}{NR},$$

$$M_i^2 = \frac{R}{B}\int\limits_0^\infty \frac{1}{w+1}\frac{df(w)}{dw}dw,$$

$w = W/B$, W is the kinetic energy of the removed electron, $df(w)/dw$ the differential oscillator strength of the molecule, N the number of electrons in the molecular orbital, $R = 13.6058$ eV is the Rydberg constant, and $a_0 = 5.2918 \times 10^{-11}$ m is the Bohr radius. In the following calculations, the value of Q was considered to be equal to 1 [9].

The expression for the ionization cross-section from the molecular orbital in the Gryziński approximation looks like

$$\sigma_i(t) = \frac{\sigma_0}{B^2}\frac{1}{t}\left(\frac{t-1}{t+1}\right)^{3/2} \times$$
$$\times \left\{1 + \frac{2}{3}\left(1 - \frac{1}{2t}\right)\ln\left[2.7 + (t-1)^{1/2}\right]\right\}, \qquad (14)$$

where $\sigma_0 = 6.56 \times 10^{-14}$ eV^2 cm^2. So one can see that the cross-section in this approximation is only determined by the binding energy B of the electron in the molecular orbital.

The molecular structure parameters that are required for calculations in the BEB model include the binding energy B, the average kinetic energy U of the electrons, and the number N of electrons in the ionized subshell. They were calculated in the DFT and HF approximations. The values calculated in the DFT (BEB-DFT) and HF (BEB-HF) approximations for the L-forms of the molecules are very close to their counterparts obtained for the D-forms. As a result, the corresponding single-ionization cross-sections almost coincide with each other (see the data in Table 3 and the discussion in work [2]). For each molecule, the ionization is possible from 29 orbitals containing 2 electrons with binding energies up to 200 eV. For instance, the binding energy for the highest orbital in the glutamine D-molecule equals -7.0022 eV in the DFT approximation, and the corresponding value for the lowest orbital amounts to -30.5612 eV. The corresponding values for the glutamic acid molecule are -7.3334 and -30.6850 eV, respectively. The single-ionization cross-section is obtained by summing up single-ionization cross-sections from all molecular orbitals.

In Fig. 5, the experimentally measured total electron-impact ionization cross-sections (from the thresholds up to 60 eV) normalized to the corresponding value calculated in the BEB-DFT model are compared with the calculated single-ionization cross-sections (from the thresholds up to 200 eV) obtained for the D-forms of the molecules. The normalization was carried out at an energy of 8.5 eV for the glutamine molecule and 9.0 eV for the glu-

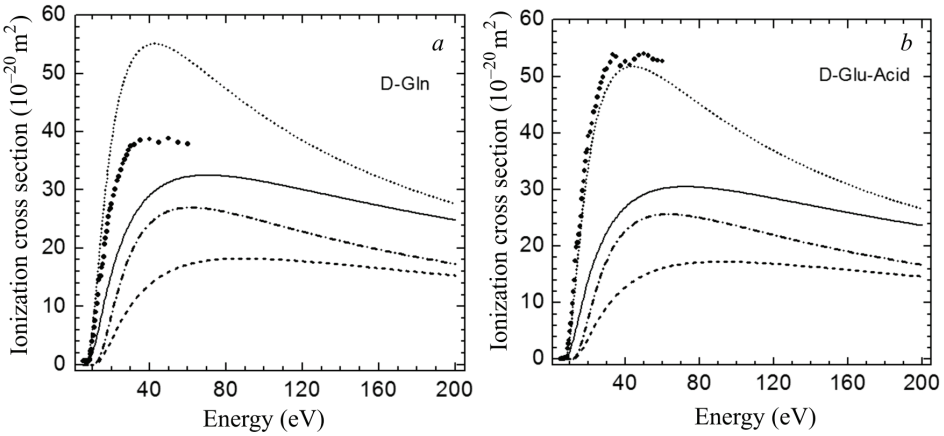


Fig. 5. Ionization cross-sections of the *D*-forms of glutamine (*a*) and glutamic acid (*b*) molecules. The symbols (●●●) correspond to experimental values normalized by the result of BEB-DFT calculations at an energy of 8.5 eV (for glutamine) or 9.0 eV (for glutamic acid). The curves demonstrate the results of theoretical calculations for the total single-ionization cross-sections: BEB-DFT (solid curves), BEB-HF (dashed curve), Gryz-DFT (dotted curves), and Gryz-HF (dash-dotted curves)

tamic acid one. We consider that, at such energies that are close to the threshold value, the total ionization cross-section is determined by the ionization cross-section of the parent molecule. The cross-sections were calculated in the framework of the BEB model [Eq. (13)] and according to the Gryzińsky formula (14) (Gryz). The parameters of the molecules calculated in the DFT and HF approximations were applied.

As one can see from Fig. 5, the BEB and Gryz cross-sections calculated using the DFT characteristics of the molecules better reproduce the initial sections in the energy dependences of the experimental ionization cross-sections than the corresponding cross-sections obtained using the HF characteristics. The ionization cross-sections calculated in the same approximations for both molecules are approximately identical by magnitude. The BEB-DFT and Gryz-DFT cross-sections are almost twice (at 60 eV) as large as the corresponding BEB-HF and Gryz-HF cross-sections. Note that the cross-sections calculated according to the Gryziński formula always exceed the corresponding BEB cross-sections. They also exceed the experimental data for the glutamine molecule and are slightly smaller than the measured ionization cross-sections for the glutamic acid molecule.

In work [35], the total electron-impact ionization cross-sections of such biomolecules as adenine ($C_5H_5N_5$) and guanine ($C_5H_5N_5O$) were measured at energies from their thresholds to 200 eV. The cited authors also estimated the magnitude of the partial cross-sections for the formation of various ionic fragments at the dissociative ionization of the indicated molecules. The energy and the total ionization cross-section at the maximum are: for adenine, 90 eV and $(2.8 \pm 0.6) \times 10^{-15}$ cm^2, respectively; and for guanine, 88 eV and $(3.2 \pm 0.7) \times 10^{-15}$ cm^2, respectively. The measured ionization energy thresholds are (8.8 ± 0.2) eV for adenine and (8.3 ± 0.2) eV for guanine. The total ionization cross-sections of the glutamine and glutamic acid molecules measured by us at an energy of 60 eV equal 3.79×10^{-15} and 5.27×10^{-15} cm^2, respectively. One sees that the ionization cross-sections and ionization thresholds of those molecules are comparable by magnitude with the data obtained for the adenine and guanine molecules. The energy dependences of the total ionization cross-sections also have a similar behavior.

The authors of work [36] used the BEB model to calculate the electron-impact single-ionization cross-sections for the uracil ($C_4H_4N_2O_2$), thymine ($C_5H_6N_2O_2$), cytosine ($C_4H_5N_3O$), adenine ($C_5H_5N_5$), and guanine ($C_5H_5N_5O$) biomolecules within an energy interval from the corresponding ionization threshold to 5 keV. They also calculated the maximum values of the single-ionization cross-sections: 2.184×10^{-15} cm^2 at an energy of 80 eV for guanine, 2.046×10^{-15} cm^2 at an energy of 75 eV for adenine, 1.761×10^{-15} cm^2 at an energy of 82 eV for thymine, 1.658×10^{-15} cm^2 at an energy of 80 eV for

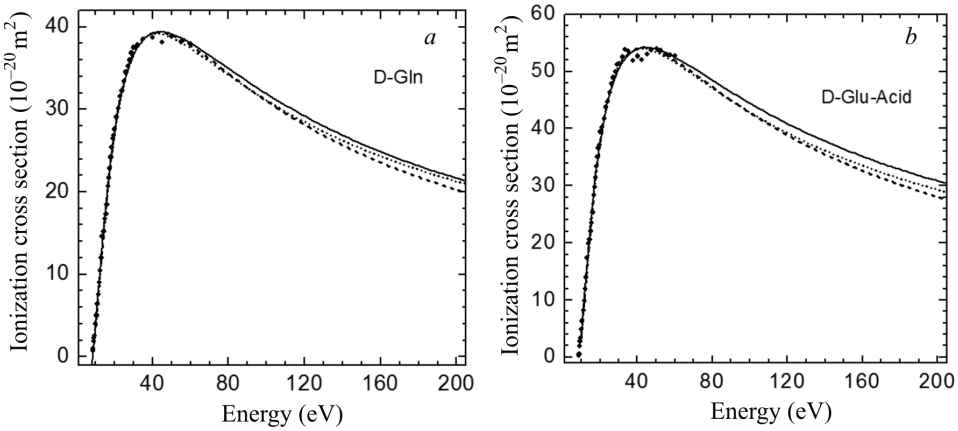


Fig. 6. Total ionization cross-sections of the D-forms of glutamine (a) and glutamic acid (b) molecules. The symbols correspond to experimental values normalized by the result of BEB-DFT calculations at an energy of 8.5 eV (for glutamine) or 9.0 eV (for glutamic acid). The curves are the results of the BED [Eq. (15), solid curves], BEB [Eq. (16), dashed curves], and Gryz [Eq. (17), dotted curves] fittings

cytosine, and 1.457×10^{-15} cm^2 at an energy of 85 eV for uracil molecules. Those data are in good agreement with the results of work [35]. They are also close to our results. In our opinion, this fact confirms that such values of the ionization cross-sections and the energies at the maximum are inherent to biomolecules.

Formulas (13) and (14), as well as a similar formula of the Binary-Encounter-Dipole (BED) model, make it possible to fit the measured cross-sections (see work [9]). In particular (see Fig. 6 below), the experimental curves obtained for the total ionization cross-sections (in 10^{-20}-m^2 units) of the D-forms of the both molecules were fitted using the following three expressions:

in the BED model,

$$\sigma_i^{\mathrm{BED}}(x) = \frac{1}{x}\left\{a\ln x + b\left(1-\frac{1}{x}\right) + c\frac{\ln x}{x+1}\right\}, \qquad (15)$$

in the BEB model,

$$\sigma_i^{\mathrm{BEB}}(x) = \\ = \frac{1}{x}\left\{a\left(1-\frac{1}{x^2}\right)\ln x + b\left(1-\frac{1}{x}\right) + c\frac{\ln x}{x+1}\right\}, \qquad (16)$$

and in the Gryziński approximation,

$$\sigma_i^{\mathrm{Gryz}}(x) = \frac{1}{x}\left(\frac{x-1}{x+1}\right)^a \times \\ \times\left\{1 + b\left(1-\frac{1}{2x}\right)\ln\left[c+(x-1)^d\right]\right\}. \qquad (17)$$

Here, $x = T/B_1$, where B_1 is the lowest electron binding energy; and a, b, c, and d are fitting parameters. Note that the first term in Eq. (15) describes the dipole interaction, and the third term was obtained by integrating the interference term in the Mott formula [9].

The fitting was carried out using the least-squares method and the experimentally measured values for the ionization thresholds: $B_1 = 8.64$ eV for Gln and 8.86 eV for Glu (Table 2). The calculated values of the fitting parameters are quoted in Table 3. One can see that, for the three-parameter fitting formulas in the BED and BEB models, the resulting fitting parameter values are rather large. Their determination errors are much smaller for the BED model. At the same time, in the case of the four-parameter Gryziński approximation, the resulting fitting parameter values are smaller by value and are characterized by small errors.

In Fig. 6, the energy behavior of the total ionization cross-sections for the D-forms of the molecules calculated within an energy interval from the ionization thresholds to 200 eV using the fitting parameters taken from Table 3 is illustrated. As one can see, all fitting curves for each molecule approximate well the experimental cross-sections and almost coincide with one another.

There is a certain difference in the behavior of the cross-sections above their maximum energy, which is reached at an electron energy of about 42–43 eV.

For both molecules, the cross-sections obtained in the BED model are the largest, and the cross-sections obtained in the BEB model are the smallest, whereas the cross-sections calculated according to the Gryziński formula fall within an interval between them. Thus, the obtained fitting parameters can be confidently used in the corresponding formulas to calculate the total ionization cross-sections for glutamine and glutamic acid molecules at intermediate and high electron energies, as well as the electron-impact ionization rates of those molecules.

5. Conclusions

It is shown that the high emergence efficiency of ionic fragments of the glutamine and glutamic acid molecules at their interaction with electrons and a strong temperature dependence of the fragment formation testify to very complicated mechanisms governing the electron-impact fragmentation of those molecules. The experimental mass spectra of the examined molecules are analyzed, and possible mechanisms giving rise to the formation of the most intensive ionic fragments owing to electron-impact dissociative ionization of the molecules weare indicated. For instance, the detachment of the carboxyl group COOH leads to the appearance of a number of intensive peaks at $m/z = 84$ and less intensive ones at $m/z = 41$ and 28. The detachment of the $C_2H_3NO_2^+$ fragment results in the appearance of ionic fragments with masses of 41 (in the case of the glutamic acid molecule) and 56 (for both molecules).

The temperature dependences of the yields of positive ionic fragments were measured in a temperature interval of 310–430 K. For the seven most intensive peaks of ionic fragments, the behavior of those dependences was analyzed. Their saturation within a temperature interval of 370–410 K is found, which is followed by a drastic decrease associated with the decay of the examined molecules and their fragments ($C_3H_2NO_2^+$, $C_3H_4O^+$), and the change in the curve slope as a result of the dissociative ionization process.

The energy dependences of the relative total cross-sections for the formation of positive ions at the electron-impact ionization of the glutamine and glutamic acid molecules were measured in an energy interval from 5 to 60 eV. Those dependences are quite similar for both molecules. They demonstrate a drastic growth of the cross-section value from the ionization threshold to an energy of about 20 eV and the presence of small cusps and irregularities. The origin of the detected features was found to be associated with the appearance of molecular ionic fragments in the course of dissociative ionization process. The ionization potentials of the molecules concerned were measured.

The ionization potentials of the parent glutamine and glutamic acid molecules were calculated in the adiabatic approximation using the density-functional-theory and Hartree–Fock methods. The calculations were based on the determination of the total energy difference between the corresponding molecular systems using the *ab initio* approach and with the help of standard quantum chemical software packages. The energy characteristics of the *L*-forms of the molecules calculated in both approaches were found to be close to the analogous values for their *D*-forms. The values calculated using the density functional theory agree well with the measured values. The ionization potentials of the examined molecules were also evaluated in the molecular orbital approximation.

The theoretical calculation of the total electron-impact single-ionization cross-sections of the *D*-forms of both molecules performed in the framework of the binary encounter Bethe model allowed the absolute values for the measured cross-sections to be obtained. The calculated values turned out close to the corresponding single-ionization cross-sections for the *L*-forms of the molecules. The molecular structural parameters determined by applying the density functional theory method and used in the cross-section calculations gave a better description for the cross-section behavior at energies below 30 eV than the parameters obtained in the Hartree–Fock approximation. The fitting of the absolute values of the total ionization cross-sections of the *D*-forms of the glutamine and glutamic acid molecules with the help of the three-parameter formulas of the BEB and BED models and the four-parameter Gryziński expression is carried out. It is shown that those formulas with the fitted parameters can be used to calculate the ionization cross-sections at high energies and the ionization rates.

It should also be noted that the mass spectrometric studies of amino acid molecules in the gas phase with the help of the electron-impact method provide a rich information concerning their unique properties. They

make it possible to determine their fragmentation degree after their interaction with electrons and evaluate the parameters of intermolecular bonds.

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А.М. Завілопуло, Ш.Ш. Демеш,
Є.Ю. Ремета, А.І. Булгакова

ІОНІЗАЦІЯ ЕЛЕКТРОНАМИ МОЛЕКУЛ ГЛЮТАМІНОВОЇ КИСЛОТИ ТА ГЛЮТАМІНУ

Проведено комплексні (експериментальні і теоретичні) дослідження виходу позитивних іонів молекул глютамінової кислоти (Glu-Acid) і глютаміну (Gln) в газовій фазі, утворених в результаті дисоціативної іонізації цих амінокислот електронним ударом. Експеримент проводився на установці з монопольним мас-спектрометром типу МХ-7304А в діапазоні масових чисел 10–150 Da. Досліджено мас-спектри молекул глютамінової кислоти і глютаміну при різних температурах, динаміку виходу іонів-фрагментів в інтервалі температур випаровування вихідної речовини 310–430 K та детально проаналізовано особливості процесів утворення іонів-фрагментів таких молекул електронним ударом. Проведено *ab initio* розрахунки потенціалів іонізації глютамінової кислоти і глютаміну в адіабатичному наближенні та за енергіями зв'язку HOMO- і LUMO-орбіталей нейтральних молекул. Отримано сумарні перерізи одноелектронної іонізації обох молекул електронним ударом в Binary-Encounter-Bethe моделі та за формулою Гризінського. Показано, що розраховані молекулярні константи добре узгоджуються з отриманими експериментальними даними.

Ключові слова: мас-спектр, амінокислота, дисоціативна іонізація, іон-фрагмент, переріз іонізації.