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Quantum chemical investigations of the fragmentation of amino acids by low energy electrons

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VILNIAUS UNIVERSITETAS

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Aminorūgščių fragmentacijos,
vykstančios dėl lėtų elektronų
poveikio, tyrimas kvantinės
chemijos metodais

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LIST OF ABBREVIATIONS

- AA – amino acid(s)
- B3LYP – Becke three-parameter hybrid functional combined with Lee–Yang–Parr correlation functional
- DFT – Density Functional Theory
- HOMO – highest occupied molecular orbital
- LUMO – lowest unoccupied molecular orbital
- NIST – National institute of standards and technology
- PCM – Polarized Continuum Model
- ZPE – Zero-point energy

INTRODUCTION

All living organisms are constantly affected by ionizing radiation emitted by natural sources, such as radionuclides contained in air, food, water and rocks from the Earth and cosmic rays. The annual global effective dose per person originating from natural ionizing radiation sources is 2.4 mSv (UNSCEAR, 2000). For example, during computed tomography of the abdomen, patients receive 10 mSv irradiation (Brenner & Hall, 2007). Therefore, humans are exposed to instantaneous irradiation doses that are naturally occur over a span of a few years.

Low-energy electrons (between 1 and 100 eV) (Hoffmann & Stroobant, 2007) are generated due to the interaction of Röntgen and gamma rays with organic molecules. These low-energy electrons damage biomolecules, including DNA (Boudaïffa et al., 2000; Barrios et al., 2002; Huels et al., 2003; Tonzani & Greene, 2006) and amino acids (AAs) (Ipolyi et al., 2006; Tamuliene et al., 2016; Farajmand & Bahrami, 2016). Low-energy electron interactions split AAs into cations, anions and neutral fragments, making them unable to perform their normal functions. For this reason, an organism's resistance to infectious diseases (Walsh et al., 1999; Li et al., 2007; Wu, 2009; Wu, 2013) and oxidative stress is decreased, and peptide, protein, hormone, purine, pyrimidine, histamine (Wu, 2009; Wu, 2013), melanin (Gordon, 2013) and neuromediator (Wu, 2009; Wu, 2013) syntheses are impaired. After AA fragmentation, haemodynamics and angiogenesis are disrupted (Wu, 2009). Furthermore, osmotic regulation, signal transduction regulation (Wu, 2009; Wu, 2013), and cell proliferation, differentiation (Wu, 2009) and apoptosis (Wu, 2009; Wu, 2013) are altered. After biomolecules are damaged, more cells than normal die. Due to cell apoptosis and necrosis, tissue and organ functions are impaired, and as a result, radiation sickness or oncological disease may occur (Forshier, 2009).

The influence of low-energy electrons on amino acid fragmentation, are investigated by mass spectrometry methods. The mass of fragments produced during fragmentation are measured experimentally. We have

been using theoretical methods to identify fragments corresponding to the most intense peaks in the experimentally measured mass spectra. The initial mass spectrometry data could help to identify processes occur in living organisms when they are exposed to ionizing radiation.

The majority of biophysical processes and biochemical reactions occur in water. Water molecules are the dominant chemical component in cells, accounting for approximately 70% of the cell weight (Palsson, 2011; Tamminen et al., 2013; Alberts et al., 2014). It is well known that in the gaseous phase, AAs are in the canonical form ($\text{NH}_2\text{-CH(R)-COOH}$), while zwitterionic conformers ($\text{NH}_3^+\text{-CH(R)-COO}^-$) prevail in water. L-glutamic acid (in water, this molecule is called L-glutamate) (Roddick-Lanzilotta & McQuillan, 2000; Latha et al., 2007) and L-aspartic acid (in water, this molecule is called L-aspartate) (Leela et al., 2012) are anionic species, while L-lysine (Roddick-Lanzilotta et al., 1998), L-arginine (Kuvaeva et al., 2012) and L-histidine (Raju et al., 2016) are positively charged in water.

It has been experimentally determined that the fragmentation degree of relatively large peptides (tetraglycine) in water is greater than that of smaller peptides (diglycine) (Ren & Kresin, 2008). Deuterated water suppresses glycine (the smallest amino acid) fragmentation more than tryptophan (the largest amino acid) fragmentation (Ren et al., 2007). Valine fragmentation in deuterated water is also suppressed (Denifl et al., 2009). Despite the enormous importance of AAs, experimental/theoretical data on the influence of water on the fragmentation of AAs are limited.

Amino acids fragmentation research results are very important not only for ionization radiation investigations (Ipolyi et al., 2006) but also for protein sequencing experiments (Armirotti et al., 2007; Bagal et al., 2016) and the post-translation modification of peptides (Nalivaeva & Turner, 2001; Hoffmann & Stroobant, 2007). In addition, knowledge about which fragments result from AA fragmentation and their appearance energies may enable the regulation of fragmentation in cells.

Aim

The main aim of this thesis is to determine whether the appearance energies and structures of fragments are different in different environments (vacuum and water).

The objectives of the thesis are as follows:

- to determine the most stable conformers of L-threonine, L-glutamic acid, L-glutamine, L-leucine and L-isoleucine in vacuum and water;
- to determine the fragment appearance energy when fragmentation due to low-energy electrons occurs in vacuum and water;
- to determine the differences in fragment structures in vacuum and water;
- to determine whether AAs with a similar mass (a difference of 1 Da) but different chemical compositions undergo fragmentation differently;
- to determine whether AAs with the same mass and chemical composition but different geometrical structures undergo fragmentation differently.

Scientific novelty

- It is determined that the fragments' appearance energy depends on the environment.
- It is determined that fragments structures' depend on the environment.
- For the first time, the chemical compositions of fragments that correspond to the most intense peaks in the L-glutamine cation mass spectrum are identified.
- This is the first study on the fragmentation of L-threonine, L-glutamine, L-leucine and L-isoleucine in water.

Defence statements

- The environment affects the appearance energy of fragments.
- AAs with a similar mass (a difference of 1 Da) but different chemical compositions undergo fragmentation in a similar manner.
- AAs with the same mass and chemical composition, but different geometrical structures undergo fragmentation in a similar manner.

In practical terms, the significance of the thesis is that the theoretically obtained results allow an interpretation of the experimentally obtained L-threonine, L-glutamic acid, L-glutamine, L-leucine and L-isoleucine cation mass spectra. The obtained results could be used in protein sequencing research. Moreover, the influence of the environment on AA fragmentation was investigated.

1. RESEARCH METHODS

Structures and fragments of the L-threonine, L-glutamic acid, L-glutamine, L-leucine and L-isoleucine molecules were studied by the Density functional theory (DFT) Becke three-parameter hybrid functional combined with Lee–Yang–Parr correlation functional (B3LYP) with correlation consistent valence triple zeta basis set (cc-pVTZ). These quantum chemical methods were used to examine the fragmentation processes of valine (Tamuliene et al., 2018), tryptophan (Tamuliene et al., 2015), asparagine (Tamuliene et al., 2014) and other AAs by low-energy electrons. The results of our theoretical research are in accord with the experimental results from our partners, i.e., the appearance energy (E_{ap}) needed to form cations coincides with the experimentally measured values with < 5% difference. For this reason, DFT B3LYP with the cc-pVTZ basis set was also selected in this work. The ,C‘ index was placed after the number of a conformer, i.e., IC, to indicate the canonical conformer, and ,Allo‘ is used to indicate the allo conformer.

The geometry of the AA structures was optimized without any symmetry restrictions until the equilibrium point was reached. The vibration frequencies of each conformer were analysed to ensure that the real equilibrium point was determined. The total energy values of the conformers at their equilibrium points were compared: L-threonine, L-glutamic acid, L-glutamine, L-leucine and L-isoleucine conformers possessing the lowest total energy were selected, as they were the most stable conformers, and they were chosen for further research on fragmentation induced by low-energy electrons. We selected only one conformer of each of Glu, Gln, Leu and Ile because the total energy of the other conformers was larger for the corresponding AA, with a total energy greater than 0.02 eV (the thermal energy, kT , at room temperature). In contrast, we found two stable Thr structures that differed in energy by 0.02 eV. For this reason, both L-threonine and L-allo-threonine fragmentations were investigated.

The bond lengths and bond orders of the L-threonine, L-glutamic acid, L-glutamine, L-leucine and L-isoleucine conformers were

analysed to determine the weakest bonds, which are most likely to be cleaved. The ‘weakest bond’ is the bond whose length increases, whereas the order decreases after ionization of the molecule (Mulliken, 1955). The ionization energy (IE) was also calculated as the difference in the energy between the positively charged AA structure and the neutral structure (Young, 2001; Smalø et al., 2010). Fragmentation occurs when the appearance energy required for the formation of the fragments is higher than IE. We calculated the adiabatic IE in all cases, excluding Thr because molecules of ionized Thr are unstable.

To select which mass cation production was investigated, in this research, the experimentally measured mass spectra of the positively charged AAs were used. Our research partners Dr. Liudmila Romanova, Dr. Vasyly Vukstich, Dr. Alexander Papp and Dr. Sci. Alexander Snegursky from the Institute of Electron Physics, National Academy of Sciences of Ukraine, experimentally obtained the L-threonine and L-glutamine cation mass spectra. They investigated low-energy (≤ 70 eV) electron interactions with Thr and Gln (temperature $< 150^\circ$ C). The energy needed to form the cations was measured. We also used positively charged ion mass spectra of L-glutamic acid, L-leucine and L-isoleucine, which are published in the National institute of standards and technology (NIST) database (viewed on 2016-06-30, 2017-03-30 and 2017-12-30, respectively). We emphasize that the NIST database does not provide information on the chemical composition of fragments, fragments appearance energy or fragmentation process.

The appearance energy of the cation was calculated as the difference between the total energy of an AA molecule and the sum of the energies of the fragments. The amount of energy needed to form positively charged fragments when the other fragment (complementary) formed during the same fragmentation process was an anion, a cation, or a neutral fragment was calculated.

Geometry optimization was performed in all cases (structures of molecules and fragments), excluding calculation of the ionization energy of L-threonine. To obtain precise conformers, fragments and appearance energies, the zero-point energy (ZPE) was included.

When the calculated appearance energy differed from the experimentally measured value at <5% error, these E_{ap} values were considered equivalent. It is predicted that cations with the lowest appearance energy are the most likely to form.

However, in several cases, the appearance energies of positively charged fragments with the same masses but with different chemical compositions were very similar (same relative error). To determine which fragment is most likely to form, we calculated several other parameters. The binding energy per atom was used to evaluate which fragment is most thermally stable. The binding energy per atom was calculated as the difference between the total energy of a positively charged fragment and the sum of the energies of the cation's H, C, N, and O elements. This difference was divided by the number of atoms in the fragment. We also calculated the electronegativity, electron affinity, chemical hardness and the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gaps to determine the chemical stability and reactivity.

As mentioned above, the medium can influence the AA structure. To investigate AA fragmentation induced by low-energy electrons in water, we performed an investigation that included the water using the polarized continuum model (PCM) (Skyner et al., 2015). The main structural differences in AAs (the positions of the hydrogens of the carboxyl and amine groups) disappeared in water, i.e., the hydrogen of the carboxyl group dissociates and attaches to the amino group. The total energy values of the zwitterionic conformers in water were compared, and the most stable conformer of each AA (the conformer with the lowest total energy) was chosen. We used the 'Z' index (IZ) to indicate that the zwitterionic molecule and its fragmentation behaviours were studied. Note that we did not study the fragment interactions or possible reactions with the medium.

Previous studies (Roddick-Lanzilotta & McQuillan, 2000; Latha et al., 2007) revealed that the form of Glu dominates over the other forms of Glu in water. Molecules with a negative charge could not undergo fragmentation caused by low-energy electrons. Hence, L-glutamate fragmentation in water was not investigated.

The influence of hydrogen bonds between AAs and H₂O on AA fragmentation was also investigated. We modelled five Thr-H₂O, Gln-H₂O, Leu-H₂O and Ile-H₂O complexes and chose the most stable of each complex. We investigated the most probable fragments production from the most stable complex for each AA fragmentation.

In this research, Gaussian 03 Rev D.01 (Gaussian 03), Gaussian 09 Rev D.01 (Gaussian 09) and Molden (5.1 and 5.9) (Gijs & Noordik, 2000) software packages were used.

2. RESULTS OF CALCULATIONS AND THEIR INTERPRETATIONS

2.1. L-threonine fragmentation

The views of the lowest energy L-threonine IC and L-allo-threonine ICAllo conformers in vacuum, the lowest energy zwitterionic IZAllo conformer in water, and the numbers of atoms used in this work, are shown in Fig. 1.

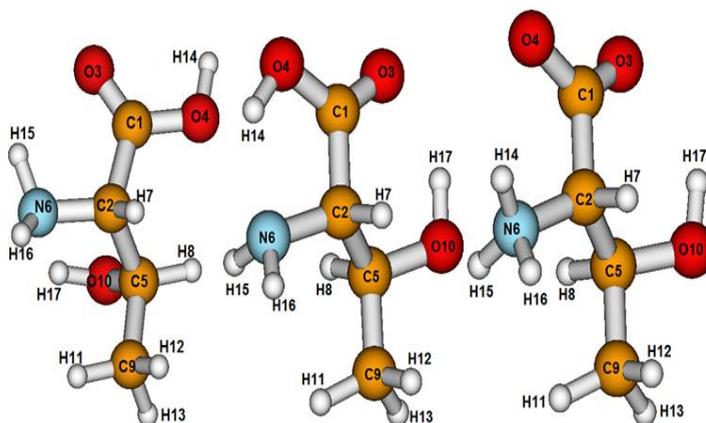


Figure 1. Views of the most stable of the studied L-threonine conformers. The L-threonine conformer IC (in vacuum) is on the left, L-allo-threonine (ICAllo) (in vacuum) is in the centre and L-allo-threonine IZAllo (in water) is in the right. The ICAllo conformer contains intermolecular hydrogen bonds between O3-H17 and N6-H14 atoms, while the IZAllo conformer contains intermolecular hydrogen bonds between O3-H17 and O4-H14.

According to our theoretical research, the weakest bond in the IC, ICAllo and IZAllo conformers is C2-C5. This bond could cleave during molecule (IC or ICAllo) ionization. Another bond that tends to rupture is C1-O3.

We also calculated the ionization energy (IC- 9.31 eV, ICAllo- 9.27 eV and IZAllo- 9.97 eV) when the ionized Thr molecule does not split. However, when the IC and ICAllo conformers are in an equilibrium state, they should be split (according to our calculation

data). Based on our results, the IE of the Thr conformers is lower in vacuum than in water, i.e., the cation appearance energy in water should be higher than that in vacuum.

As mentioned above, the mass spectrum of the L-threonine cation measured by our colleagues it used (it will be published in article in the near future). The calculated appearance energies (in eV) needed for the formation of cations in vacuum are presented in Table 1.

Table 1. Calculated appearance energies (in eV) of cations formed from the Thr IC and ICAllo conformers in vacuum

Cation	Complementary fragment (when Thr IC undergoes fragmentation)	Complementary fragment (when Thr ICAllo undergoes fragmentation)	Thr IC	Thr ICAllo
			Appearance energy, eV	
CH ₃ N ⁺ (m/z=29)		C ₃ H ₆ O ₃	10.20	10.55
CH ₄ N ⁺ (m/z=30)	-	C ₃ H ₅ O ₃ ⁰	-	8.76
CH ₂ O ⁺ (m/z=30)		C ₃ H ₇ NO ₂ ⁰	11.63	11.81
CH ₃ O ⁺ (m/z=31)		C ₃ H ₆ NO ₂ ⁻	11.58	8.19
CH ₆ N ⁺ (m/z=32)		C ₃ H ₃ O ₃ ⁰	9.05	8.77
CH ₄ O ⁺ (m/z=32)	C ₃ H ₅ NO ₂ ⁻	C ₃ H ₅ NO ₂ ⁰	12.18	12.53
C ₂ H ₃ N ⁺ (m/z=41)		C ₂ H ₆ O ₃ ⁰	10.22	11.06
C ₂ H ₂ O ⁺ (m/z=42)	C ₂ H ₇ NO ₂ ⁰	C ₂ H ₇ NO ₂ ⁻	9.46	11.92
C ₂ H ₃ O ⁺ (m/z=43)		C ₂ H ₆ NO ₂ ⁻	8.96	10.67
C ₂ H ₆ N ⁺ (m/z=44)	-	C ₂ H ₃ O ₃ ⁰	-	8.93
CO ₂ ⁺ (m/z=44)		C ₃ H ₉ NO ⁰	13.23	13.48

Table 1 continues on the next page

Table 1 (continued)

Cation	Complementary fragment (when Thr IC undergoes fragmentation)	Complementary fragment (when Thr ICAllo undergoes fragmentation)	Thr IC	Thr ICAllo
			Appearance energy, eV	
$C_2H_5O^+$ (m/z=45)		$C_2H_4NO_2^-$	9.03	8.41
CHO_2^+ (m/z=45)		$C_4H_9NO_3^0$	11.39	11.44
$C_2H_6O^+$ (m/z=46)		$C_2H_3NO_2^-$	10.80	10.79
$C_2H_3NO^+$ (m/z=57)		$C_2H_6O_2^-$	11.79	11.59
$C_2H_3NO^+$ (m/z=57)		$C_2H_6O_2^-$	11.79	11.59
$C_3H_5O^+$ (m/z=57)	$CH_4NO_2^0$	$CH_4NO_2^-$	10.12	8.70
$C_3H_7N^+$ (m/z=57)		$CH_2O_3^-$	8.86	8.82
$C_2H_4NO^+$ (m/z=58)	$C_2H_5O_2^0$	$C_2H_5O_2^-$	8.57	9.02
$C_3H_6O^+$ (m/z=58)	$CH_3NO_2^0$	$CH_3NO_2^-/$ $CH_3NO_2^0$	8.40	8.55/ 8.60
$C_2H_2O_2^+$ (m/z=58)	-	$C_2H_7NO^0$	-	12.80
$C_2H_5NO^+$ (m/z=59)	$C_2H_4O_2^-$	$C_2H_4O_2^0$	9.30	8.00
$C_3H_7O^+$ (m/z=59)		$CH_2NO_2^0$	8.61	8.63
$C_3H_6N^+$ (m/z=59)		CO_3^-	8.88	8.00
$C_3H_8NO^+$ (m/z=74)	CHO_2^0	CHO_2^-	8.79	8.24
$C_2H_4NO_2^+$ (m/z=74)		$C_2H_5O^0$	9.41	-
$C_3H_9NO^+$ (m/z=75)		CO_2^0	8.77	8.18
$C_2H_5NO_2^+$ (m/z=75)	$C_2H_4O^-$	$C_2H_4O^0$	9.29	-

It was determined that the fragment at $m/z=29$ is CH_3N^+ (Table 1). According to our results, the $m/z=30$ cation formed during Thr IC fragmentation is CH_2O^+ . When ICAllo undergoes splitting into fragments, CH_4N^+ ($m/z=30$) is produced. We found that fragment at $m/z=31$ is CH_3O^+ , $m/z=32$ is CH_6N^+ , $m/z=41$ is $\text{C}_2\text{H}_3\text{N}^+$, $m/z=42$ is $\text{C}_2\text{H}_2\text{O}^+$, and $m/z=43$ is $\text{C}_2\text{H}_3\text{O}^+$. According to our investigation results, $m/z=44$ is CO_2^+ (in the IC conformer case) and $\text{C}_2\text{H}_6\text{N}^+$ (in the ICAllo conformer case).

We determined that in the case of IC conformer fragmentation, $\text{C}_2\text{H}_5\text{O}^+$ ($m/z=45$) fragment formation requires less energy (9.03 eV) than the formation of CHO_2^+ ($m/z=45$) (Table 1). Furthermore, the $\text{C}_2\text{H}_5\text{O}^+$ ($m/z=45$) formation during ICAllo fragmentation requires less energy (8.41 eV) than that required to form CHO_2^+ ($m/z=45$, $E_{\text{ap}}=11.44$ eV). Our collaborators measured the appearance energy of this mass fragment as 11.50 ± 0.1 eV. A comparison of the calculated appearance energy values and the experimentally measured values for the cations with $m/z=45$ suggest that the peak in the positively charged ion mass spectrum could be CHO_2^+ .

We determined that the peak at $m/z=46$ could be identified as $\text{C}_2\text{H}_6\text{O}^+$.

The formation of $\text{C}_2\text{H}_3\text{NO}^+$ ($m/z=57$), $\text{C}_3\text{H}_5\text{O}^+$ ($m/z=57$) and $\text{C}_3\text{H}_7\text{N}^+$ ($m/z=57$) was investigated. We established that $\text{C}_3\text{H}_7\text{N}^+$ ($m/z=57$) could form during IC fragmentation. $\text{C}_3\text{H}_5\text{O}^+$ ($m/z=57$) and $\text{C}_3\text{H}_7\text{N}^+$ ($m/z=57$) may form during ICAllo fragmentation, i.e., their appearance energy is approximately equal. On the other hand, our calculated appearance energy of $\text{C}_2\text{H}_3\text{NO}^+$ (Table 1) and that measured by our collaborators (12.00 ± 0.1 eV) are in agreement. Hence, $\text{C}_2\text{H}_3\text{NO}^+$ ($m/z=57$) is the most likely to be formed among these cations.

The fragment at $m/z=58$ could be $\text{C}_2\text{H}_4\text{NO}^+$, $\text{C}_3\text{H}_6\text{O}^+$ or $\text{C}_2\text{H}_2\text{O}_2^+$ (Table 1). In this molecular modelling research, the calculated appearance energies of $\text{C}_2\text{H}_4\text{NO}^+$ ($m/z=58$) and $\text{C}_3\text{H}_6\text{O}^+$ ($m/z=58$) are in agreement. The binding energy per atom (thermal stability) of these fragments is also in agreement: it is 3.78 eV for $\text{C}_2\text{H}_4\text{NO}^+$ and 3.69 eV for $\text{C}_3\text{H}_6\text{O}^+$. According to these data, the fragments at

$m/z=58$ were identified as $C_2H_4NO^+$ and $C_3H_6O^+$. In contrast, $C_2H_2O_2^+$ ($m/z=58$) should not be produced when the IC conformer undergoes fragmentation (see Table 1), and its production is not probable during ICAllo fragmentation because this process needs much more energy than the production of the other mentioned fragments (Table 1).

Based on the results of the theoretical investigation, $C_3H_7O^+$ ($m/z=59$) and $C_3H_9N^+$ ($m/z=59$) formation (in the IC case) had a lower E_{ap} than $C_2H_5NO^+$ ($m/z=59$). During ICAllo fragmentation, the $C_2H_5NO^+$ ($m/z=59$) and $C_3H_9N^+$ ($m/z=59$) appearance energies are the same (8.00 eV). To establish the chemical composition of the $m/z=59$ cation, we calculated the binding energy per atom of these cations (Table 2).

The difference between the binding energies per atom of the $C_3H_7O^+$ ($m/z=59$) and $C_3H_9N^+$ ($m/z=59$) cations is 0.06 eV (IC fragmentation case), whereas that between $C_2H_5NO^+$ ($m/z=59$) and $C_3H_9N^+$ ($m/z=59$) is 0.07 eV (ICAllo fragmentation case). Hence, the thermal stabilities of $C_3H_7O^+$ ($m/z=59$) and $C_3H_9N^+$ ($m/z=59$) are very similar (IC case); $C_2H_5NO^+$ ($m/z=59$) and $C_3H_9N^+$ ($m/z=59$) (ICAllo case) are also very similar. Therefore, $C_3H_7O^+$ ($m/z=59$) and $C_3H_9N^+$ ($m/z=59$) could form during IC fragmentation, while $C_2H_5NO^+$ ($m/z=59$) and $C_3H_9N^+$ ($m/z=59$)— could form during ICAllo fragmentation.

Table 2. Calculated binding energy per atom of cations $C_2H_5NO^+$ ($m/z=59$), $C_3H_7O^+$ ($m/z=59$) and $C_3H_9N^+$ ($m/z=59$) formed from the fragmentation of Thr IC and ICAllo conformers in vacuum

Cation $m/z=59$	IC	ICAllo
	Binding energy per atom, eV	
$C_2H_5NO^+$	3.68	3.69
$C_3H_7O^+$	3.66	3.66
$C_3H_9N^+$	3.60	3.62

The cation at $m/z=74$ could be $C_3H_8NO^+$ or $C_2H_4NO_2^+$. We calculated that the lowest appearance energies are 8.79 eV and 9.41 eV, respectively (IC case), whereas $C_3H_8NO^+$ ($m/z=74$) fragment

formation requires 8.24 eV (ICALlo case). In contrast, $C_2H_4NO_2^+$ ($m/z=74$) should not be produced during ICAllo fragmentation (see Table 1). According to these results (Table 1), it could be argued that $m/z=74$ represents $C_3H_8NO^+$. On the other hand, all these E_{ap} values do not agree with the experimentally measured $m/z=74$ cation appearance energy (11.50 ± 0.1 eV) within a statistical error margin (5%). The smallest differences between the experimentally measured and theoretically calculated E_{ap} values are in the cases where: the E_{ap} is 10.06 eV ($C_2H_4NO_2^+$ and $C_2H_5O^+$ produced during IC fragmentation) and 10.62 eV ($C_2H_4NO_2^+$ and $C_2H_5O^{+0}$ produced during ICAllo fragmentation). These values (10.06 eV/10.62 eV) are the most likely values, despite the $\sim 13\%$ and $\sim 8\%$, respectively differences between the theoretically calculated value and the measured appearance energy value. Hence, we conclude that $C_2H_4NO_2^+$ ($m/z=74$) production is more likely than $C_3H_8NO^+$ ($m/z=74$) production.

We modelled $C_3H_9NO^+$ ($m/z=75$) and $C_2H_5NO_2^+$ ($m/z=75$) cation production. According to our calculation results (Table 1), the energy required to produce $C_3H_9NO^+$ ($m/z=75$) ions is smaller than that required to produce $C_2H_5NO_2^+$ ($m/z=75$). We decided to verify whether the $m/z=75$ cation is $C_3H_9NO^+$. We calculated the binding energy per atom of the abovementioned fragments, their HOMO-LUMO gap, and the chemical hardness (Table 3).

Table 3. Calculated binding energy per atom, HOMO-LUMO gap, and chemical hardness values of cations $C_3H_9NO^+$ ($m/z=75$) and $C_2H_5NO_2^+$ ($m/z=75$), which were formed from the fragmentation of Thr IC and ICAllo conformers in vacuum

Cation $m/z=75$	IC conformer		ICALlo conformer	
	$C_3H_9NO^+$	$C_2H_5NO_2^+$	$C_3H_9NO^+$	$C_2H_5NO_2^+$
Binding energy per atom, eV	3.60	3.70	3.64	-
HOMO-LUMO gap, eV	5.61	2.22	4.67	-
Chemical hardness, eV	5.65	5.07	5.30	-

Based on the results (Table 3), the thermal stabilities of $C_3H_9NO^+$ ($m/z=75$) and $C_2H_5NO_2^+$ ($m/z=75$) are similar. However, the chemical stability of $C_3H_9NO^+$ ($m/z=75$) is greater (the HOMO-LUMO gap is higher) than that of $C_2H_5NO_2^+$ ($m/z=75$), and has a lower tendency than $C_2H_5NO_2^+$ ($m/z=75$) to participate in chemical reactions (the chemical hardness value of $C_3H_9NO^+$ is higher).

Hence, the chemical composition of the ion at $m/z=75$ is $C_3H_9NO^+$. The difference between the total energy values of the L-threonine IZ and L-allo-threonine IZAllo conformers is higher than 0.02 eV. The total energy for Thr IZAllo is smaller than that for Thr IZ. For this reason, we investigated only Thr IZAllo fragmentation by low-energy electrons. Further, the E_{ap} needed to produce cations from IZAllo (Fig. 1) in water is presented (Table 4).

Table 4. Calculated appearance energies (in eV) of cations formed from the Thr IZAllo conformer in water

Cation	Complementary fragment	Appearance energy, eV
CH_3N^+ ($m/z=29$)	$C_3H_6O_3^0$ ($m/z=90$)	11.32
CH_4N^+ ($m/z=30$)	$C_3H_5O_3^-$ ($m/z=89$)	9.32
CH_3O^+ ($m/z=31$)	$C_3H_6NO_2^-$ ($m/z=88$)	12.19
CH_6N^+ ($m/z=32$)	$C_3H_3O_3^0$ ($m/z=87$)	9.56
$C_2H_3N^+$ ($m/z=41$)	$C_2H_6O_3^0$ ($m/z=78$)	11.79
$C_2H_2O^+$ ($m/z=42$)	$C_2H_7NO_2^-$ ($m/z=77$)	13.01
$C_2H_3O^+$ ($m/z=43$)	$C_2H_6NO_2^-$ ($m/z=76$)	11.43
$C_2H_6N^+$ ($m/z=44$)	$C_2H_3O_3^0$ ($m/z=75$)	9.51

Table 4 continues on the next page

Table 4 (continued)

Cation	Complementary fragment	Appearance energy, eV
CHO_2^+ (m/z=45)	$\text{C}_3\text{H}_8\text{NO}^0$ (m/z=74)	12.36
$\text{C}_2\text{H}_6\text{O}^+$ (m/z=46)	$\text{C}_2\text{H}_3\text{NO}_2^-$ (m/z=73)	11.62
$\text{C}_2\text{H}_3\text{NO}^+$ (m/z=57)	$\text{C}_2\text{H}_6\text{O}_2^-$ (m/z=62)	12.41
$\text{C}_3\text{H}_6\text{O}^+$ (m/z=58)	CH_3NO_2^0 (m/z=61)	9.46
$\text{C}_2\text{H}_5\text{NO}^+$ (m/z=59)	$\text{C}_2\text{H}_4\text{O}_2^0$ (m/z=60)	9.83
$\text{C}_2\text{H}_4\text{NO}_2^+$ (m/z=74)	$\text{C}_2\text{H}_5\text{O}^-$ (m/z=45)	11.43
$\text{C}_3\text{H}_9\text{NO}^+$ (m/z=75)	CO_2^0 (m/z=44)	9.22

It was determined that the same cation with a certain mass and chemical composition is most likely produced in vacuum and in water. The fact that the same bonds (C2-C5 and C1-O3) are the weakest in both the ThrAllo IC and ThrAllo IZ conformers could explain why cations with the same chemical composition are the most likely cations to form in vacuum and in water.

A comparison of cation production in vacuum and in water revealed several differences. Our research results indicate that the appearance energy needed for the production of positively charged fragments with the same mass and chemical composition is lower for the decomposition of the ThrAllo IC conformer in vacuum than for the fragmentation of the ThrAllo IZ conformer in water.

It was also determined that CH_4N^+ (m/z=30) and $\text{C}_2\text{H}_6\text{N}^+$ (m/z=44) cation structures are different when they are produced by ThrAllo IC fragmentation in vacuum and when they are produced by ThrAllo IZ fragmentation in water. Based on our results, H atom migration between amino and carboxyl groups does not occur in vacuum/in water, i.e., these cations that form from the $\text{NH}_2\text{-CH(R)-COOH}$

structure in vacuum contain NH_2 and COOH groups, which form from the $\text{NH}_3^+ \text{-CH(R)-COO}^-$ in water— NH_3^+ and COO^- groups in water.

2.2. L-glutamic acid fragmentation

The most stable L-glutamic acid conformer (Fig. 2) is presented. We established that the IC conformer IE=8.93 eV (the molecular and ionized forms are in equilibrium). The weakest bond is the C5-C6.

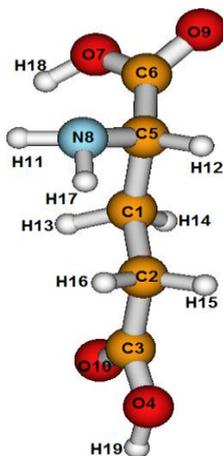


Figure 2. View of the most stable L-glutamic acid IC conformer.

The most intense peaks in the mass spectrum of L-glutamic acid correspond to $m/z=28$, 41, 56 and 84 (NIST, viewed on 2016-06-30). The calculated appearance energies (in eV) needed to determine the formation of the positively charged ions at different masses from the IC conformer in vacuum are below.

Based on our theoretical research results (Table 5), the $m/z=28$ cation could be CH_2N^+ or C_2H_4^+ . The appearance energy of these fragments agrees within the error margin. The calculated binding energy per atom was determined for CH_2N^+ (2.30 eV) and C_2H_4^+ (2.72 eV), and the HOMO-LUMO gap is 6.13 eV for CH_2N^+ ($m/z=28$) and 5.68 eV for C_2H_4^+ ($m/z=28$). Hence, the thermal stability

of $C_2H_4^+$ ($m/z=28$) is higher than that of CH_2N^+ ($m/z=28$), whereas the chemical stability of CH_2N^+ ($m/z=28$) is higher than that of $C_2H_4^+$ ($m/z=28$). Overall, it is likely that both cations are produced due to low-energy electrons.

Table 5. Calculated appearance energy, binding energy per atom and HOMO-LUMO gap values of the cations CH_2N^+ ($m/z=28$) and $C_2H_4^+$ ($m/z=28$), which might be formed from the fragmentation of the Glu IC conformer in vacuum

Cation	Complementary fragment	Appearance energy, eV	Binding energy per atom, eV	HOMO-LUMO gap, eV
CH_2N^+ ($m/z=28$)	$C_4H_7O_4^-$ ($m/z=119$)	11.62	2.30	6.13
$C_2H_4^+$ ($m/z=28$)	$C_3H_5NO_4^0$ ($m/z=119$)	11.10	2.72	5.68

It is determined that the $m/z=41$ fragment could be C_2HO^+ or $C_2H_3N^+$; i.e., their appearance energies are approximately equal (Table 6). For this reason, we evaluated the stability of these cations. The binding energy per atom is 2.60 eV (C_2HO^+) and 3.20 eV ($C_2H_3N^+$), while the HOMO-LUMO gap is 2.27 eV (C_2HO^+) and 5.60 eV ($C_2H_3N^+$). Therefore, $C_2H_3N^+$ ($m/z=41$) is more stable than C_2HO^+ ($m/z=41$) both thermally and chemically, and therefore, this cation should be dominant.

Table 6. Calculated appearance energy, binding energy per atom and HOMO-LUMO gap values of the cations C_2HO^+ ($m/z=41$) and $C_2H_3N^+$ ($m/z=41$), which might be formed from the fragmentation of the Glu IC conformer in vacuum

Cation	Complementary fragment	Appearance energy, eV	Binding energy per atom, eV	HOMO-LUMO gap, eV
C_2HO^+ ($m/z=41$)	$C_5H_9NO_4^-$ ($m/z=106$)	12.43	2.60	2.27
$C_2H_3N^+$ ($m/z=41$)	$C_3H_6O_4^-$ ($m/z=106$)	12.77	3.20	5.60

We calculated that the appearance energy needed for the formation of $C_3H_6N^+$ ($m/z=56$) is smaller than that needed for the formation of $C_3H_4O^+$ ($m/z=56$) (9.89 eV and 10.51 eV, respectively). Therefore, the peak at $m/z=56$ was identified as $C_3H_6N^+$ ($m/z=56$), while the complementary fragment is $C_2H_3O_4^0$.

We determined that the chemical composition of the $m/z=84$ fragment is $C_4H_6NO^+$. Based on our results, $m/z=84$ production requires a smaller appearance energy than the other ions of Glu, and this cation is the most likely produced of the cations studied. The most intense peak in the experimentally measured mass spectrum of Glu cations also corresponds to $m/z=84$ (NIST, viewed on 2016-06-30).

2.3. L-glutamine fragmentation

The most stable L-glutamine structures IC (in vacuum) and IZ (in water) and the numbers of atoms used in this work are presented in Fig. 3.

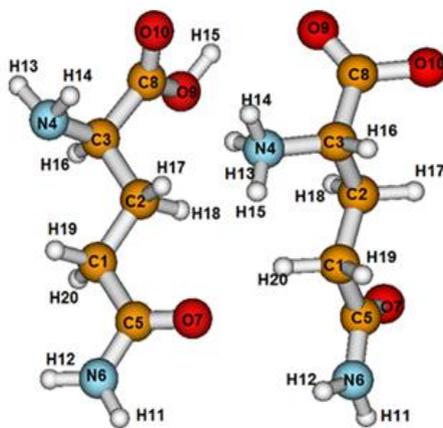


Figure 3. Views of the most stable L-glutamine conformers. The IC conformer (in vacuum) is on the left, while the IZ conformer (in water) is on the right. The IZ conformer contains an intermolecular hydrogen bond between the O9-H14 atoms.

The L-glutamine IE value was calculated to be 8.52 eV.

As mentioned above, we used the mass spectrum of positively charged L-glutamine fragments measured by our colleagues (published in (Tamuliene et al., 2019)). The $m/z=28$ cation could be CH_2N^+ (HC-NH^+) or CO^+ . We determined that the E_{ap} value of the HC-NH fragment is 13.52 eV (also forming complementary ($\text{NH}_2\text{COCH}_2\text{CH}_2 + \text{COOH} + \text{H}$)) and 13.93 eV (also forming complementary ($\text{NH}_2\text{COCH}_2\text{CH}_2 + \text{COOH} + \text{H}$)⁰). Our research partners measured the $m/z=28$ fragment appearance energy is 13.90 ± 0.1 eV. The theoretically calculated and experimentally measured fragment appearance energies agree very well. The appearance energy of the CO^+ ($m/z=28$) cation is more larger (at least 14.93 eV).

According to our theoretical research results, the $m/z=41$ fragment could be C_3H_5^+ , $\text{C}_2\text{H}_3\text{N}^+$ or C_2HO^+ . The calculated appearance energy, the binding energy per atom of the abovementioned fragments, chemical hardness and HOMO-LUMO gap are presented in Table 7.

Table 7. Calculated appearance energy, binding energy per atom, chemical hardness and HOMO-LUMO gap values of the cations C_3H_5^+ ($m/z=41$), $\text{C}_2\text{H}_3\text{N}^+$ ($m/z=41$) and C_2HO^+ ($m/z=41$), which might be formed from the fragmentation of the Gln IC conformer in vacuum

Cation $m/z=41$	Appear- ance energy, eV	Binding energy per atom, eV	Chemical hardness, eV	HOMO- LUMO gap, eV
C_3H_5^+ ($\text{CH}_2\text{CHCH}_2^+$)	9.74	3.26	2.62	2.27
$\text{C}_2\text{H}_3\text{N}^+$ (NHCCH_2^+)	10.34	2.93	3.47	6.93
C_2HO^+ (OCCH^+)	13.13	2.46	1.13	2.27

Based on the theoretically obtained results (Table 7), C_3H_5^+ has the highest thermal stability of the cations ($m/z=41$), while its E_{ap} is the smallest. However, the HOMO-LUMO gap and chemical hardness of $\text{C}_2\text{H}_3\text{N}^+$ ($m/z=41$) is the highest, so $\text{C}_2\text{H}_3\text{N}^+$ ($m/z=41$) is the most

chemically stable among these cations. On the one hand, according to these data (Table 7), $C_3H_5^+$ ($m/z=41$) and $C_2H_3N^+$ ($m/z=41$) production are probable. On the other hand, the E_{ap} values of these fragments are above the margin of error from the value of 12.20 ± 0.1 eV measured by our colleagues. For this reason, the cascade process was investigated, i.e., the process where the $C_4H_6NO^-$ ($m/z=84$) anion was first produced, and then $C_3H_5^+$ ($m/z=41$) was produced from $C_4H_6NO^-$ ($m/z=84$). The appearance energy needed to form $C_3H_5^+$ ($m/z=41$) during the abovementioned process is 11.92 eV. This value is in agreement with the experimentally measured E_{ap} . Hence, the theoretical results indicate that $C_3H_5^+$ ($m/z=41$) production is less likely to occur during direct L-glutamine fragmentation induced by low-energy electrons than via cascade process. We believe that an experimental investigation of this cascade process could be the next step in this research.

We also determined that the $m/z=56$ cation is $C_2H_2NO^+$. The experimentally obtained appearance energy for the $m/z=56$ fragment is 13.30 ± 0.1 eV, while the theoretically calculated value is 12.12 eV. This value (12.12 eV) is the most likely value, despite the $\sim 9\%$ difference between the theoretically calculated value and the measured appearance energy value. The appearance energy needed to form $C_2H_2NO^+$ during other (~ 50) fragmentation processes differs much more than $\sim 9\%$ from the experimental value.

The most intense peak in the L-glutamine positively charged fragment mass spectrum is at $m/z=84$. This cation could be $C_4H_8N_2^+$ (the smallest $E_{ap}=8.86$ eV) or $C_4H_6NO^+$ (the smallest $E_{ap}=9.84$ eV). We determined that the $C_4H_8N_2^+$ cation appearance energy (8.86 eV) is close to our collaborator's measured value of 8.50 ± 0.1 eV. Hence, the $m/z=84$ cation could be identified as $C_4H_8N_2^+$.

A peak at $m/z=129$ is also observed in the Gln mass spectrum measured by our research partners. The fragment with $m/z=129$ can be linear or have a cyclic structure, e.g., pyroglutamic acid. The main peaks in the Gln (Tamuliene et al., 2019) and pyroglutamic acid (Cannington & Ham, 1979) mass spectra are similar, i.e., they

correspond to $m/z=28$, 41, 56 and 84. On the other hand, the peaks at $m/z=16$, 18 and 101 are observed only in the positively charged Gln ion mass spectrum. The cation at $m/z=101$ is produced after COOH group dissociation from Gln. The fragment at $m/z=18$ is water, while that at $m/z=16$ is NH_2^+ . It was established that only neutral (not positively charged) pyroglutamic acid could form from L-glutamine. The peak at $m/z=129$ is weak in the experimentally measured Gln cation mass spectrum. It is also determined that $m/z=28$, 41, 56 and 84 could be produced from only Gln, not from pyroglutamic acid.

We calculated an IE of 8.97 eV for Gln IZ. The appearance energies needed to form positively charged fragments ($m/z=28$, 41, 56 and 84) are presented in Table 8.

Table 8. Calculated appearance energies (in eV) of cations formed from the Gln IZ conformer in water

Cation	Complementary fragment	Appearance energy, eV
CH_2N^+ ($m/z=28$)	$\text{C}_4\text{H}_8\text{NO}_3^-$ ($m/z=118$)	14.79
C_3H_5^+ ($m/z=41$)	$\text{C}_2\text{H}_5\text{N}_2\text{O}_3^-$ ($m/z=105$)	12.79
$\text{C}_2\text{H}_2\text{NO}^+$ ($m/z=56$)	$\text{C}_3\text{H}_8\text{NO}_2^0$ ($m/z=90$)	12.98
$\text{C}_4\text{H}_8\text{N}_2^+$ ($m/z=84$)	CH_2O_3^- ($m/z=62$)	9.37

We determined that more energy is needed for the formation of the same fragments in water than in vacuum. We also noted that the $\text{C}_4\text{H}_8\text{N}_2^+$ ($m/z=84$) cation structure is different in vacuum and in water. This fragment in vacuum contains NH_2 and COOH groups, while when formed from $\text{NH}_3^+-\text{CH}(\text{R})-\text{COO}^-$ in water, containing NH_3^+ and COO^- groups.

2.4. L-leucine fragmentation

The most stable structures of Leu conformers, IC (in vacuum) and IZ (in water), are presented in Fig. 4.

Based on our theoretical research results, the weakest bond of the IC and IZ conformers is the C5-C6. Another weak bond is C2-C4. We also calculated that the IE of the IC conformer in vacuum is 8.50 eV. The Leu IZ IE value is 9.11 eV in water.

We used the mass spectrum for the L-leucine positively charged cation published in the NIST database (viewed on 2017-03-30) and the E_{ap} values measured by (Papp et al., 2012). According to data published in the abovementioned references, $m/z=28$, 30, 41, 43, 44, 74 and 86 cations could be produced during Leu fragmentation. Papp et al. (2012) established that $m/z=29$, 42, 57, 69, 70 and 75 fragments could be produced as well. We identified the chemical composition of all these cations and calculated their appearance energy.

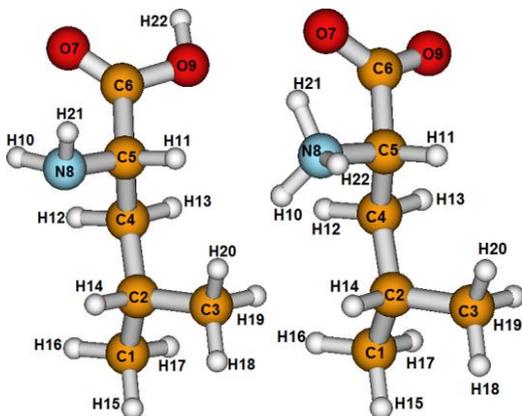


Figure 4. Views of the most stable L-leucine conformers. The IC conformer (in vacuum) is on the left, while the IZ conformer (in water) is on the right.

We investigated the possibility of producing CH_2N^+ ($m/z=28$) and C_2H_4^+ ($m/z=28$) cations, i.e., calculated their appearance energy, binding energy per atom and HOMO-LUMO gaps (Table 9). Our results indicate that the production of CH_2N^+ ($m/z=28$) cations requires a lower appearance energy (9.61 eV) than C_2H_4^+ ($m/z=28$),

and CH_2N^+ is more stable both thermally and chemically than C_2H_4^+ (Table 9). However, the E_{ap} measured by (Papp et al., 2012) is larger (13.53 ± 0.05 eV) than the value that we obtained. The appearance energy (12.98 eV) required to form C_2H_4^+ ($m/z=28$) is closer to the E_{ap} measured by the abovementioned authors. Hence, the $m/z=28$ cation could be either CH_2N^+ or C_2H_4^+ (which should be the dominant form).

Table 9. Calculated appearance energy, binding energy per atom and HOMO-LUMO gap values of the cations CH_2N^+ ($m/z=28$) and C_2H_4^+ ($m/z=28$), which might be formed from the fragmentation of the Leu IC conformer in vacuum

Cation $m/z=28$	Appearance energy, eV	Binding energy per atom, eV	HOMO-LUMO gap, eV
CH_2N^+	9.61	2.86	10.97
C_2H_4^+	12.98	2.72	5.96

We investigated whether the $m/z=29$ cation could be CH_3N^+ , C_2H_5^+ or CHO^+ . The calculation results are presented in Table 10.

Table 10. Calculated appearance energy, binding energy per atom and HOMO-LUMO gap values of the cations CH_3N^+ ($m/z=29$), C_2H_5^+ ($m/z=29$) and CHO^+ ($m/z=29$), which might be formed from the fragmentation of the Leu IC conformer in vacuum

Cation $m/z=29$	Appearance energy, eV	Binding energy per atom, eV	HOMO-LUMO gap, eV
CH_3N^+	11.44	2.59	7.96
C_2H_5^+	13.24	2.86	8.97
CHO^+	12.47	1.19	8.94

Based on our results (Table 10), less energy is needed for CH_3N^+ ($m/z=29$) than for $\text{C}_2\text{H}_5^+/\text{CHO}^+$ ($m/z=29$) production. On the other hand, the thermal and chemical stabilities of C_2H_5^+ ($m/z=29$) are higher than those of CH_3N^+ , and its appearance energy agrees with the experimentally measured value (12.98 ± 0.05 eV) determined by (Papp et al., 2012). CHO^+ ($m/z=29$) is also more chemically stable than CH_3N^+ ($m/z=29$), and the appearance energy is close to

the experimentally measured value. Therefore, CH_3N^+ ($m/z=29$), C_2H_5^+ ($m/z=29$) and CHO^+ ($m/z=29$) could be produced during Leu fragmentation. According to our results, the C_2H_5^+ ($m/z=29$) cation (complementary ion— $\text{C}_4\text{H}_8\text{NO}_2^-$) should be the dominant cation.

We established that the $m/z=30$ cation is CH_4N^+ (complementary fragment is $\text{C}_3\text{H}_9\text{O}_2^-$). The appearance energy that we calculated for this fragment is 10.79 eV. The E_{ap} we determined coincides with the $E_{\text{ap}}=10.93\pm 0.05$ eV determined by (Papp et al., 2012).

We checked the possibilities of C_3H_5^+ ($m/z=41$), $\text{C}_2\text{H}_3\text{N}^+$ ($m/z=41$) and C_2HO^+ ($m/z=41$) formation. We noticed that the lowest appearance energy among these cations is for the formation of C_3H_5^+ (complementary fragment— $\text{C}_3\text{H}_8\text{NO}_2^-$). Moreover, this cation is the most thermally stable among the three cations (Table 11). Papp et al. (2012) measured an $E_{\text{ap}}=12.31\pm 0.05$ eV, and our calculated value of 12.87 eV is in good agreement.

Table 11. Calculated appearance energy and binding energy per atom of the cations C_3H_5^+ ($m/z=41$), $\text{C}_2\text{H}_3\text{N}^+$ ($m/z=41$) and C_2HO^+ ($m/z=41$), which might be formed from the fragmentation of the Leu IC conformer in vacuum

Cation $m/z=41$	Appearance energy, eV	Binding energy per atom, eV
C_3H_5^+	12.87	3.59
$\text{C}_2\text{H}_3\text{N}^+$	13.64	3.18
C_2HO^+	14.40	2.60

We determined that the $m/z=42$ cation is C_3H_6^+ ($E_{\text{ap}}=12.43$ eV), while the complementary fragment is $\text{C}_3\text{H}_7\text{NO}_2^0$. However, $\text{C}_2\text{H}_2\text{O}^+$ ($m/z=42$) production is less probable than C_3H_6^+ ($m/z=42$) production because of its $E_{\text{ap}}=14.36$ eV. Moreover, the E_{ap} of C_3H_6^+ is in good agreement with the $E_{\text{ap}}=12.16\pm 0.05$ eV measured by (Papp et al., 2012) and C_3H_6^+ is thermally more stable (its binding energy per atom is 3.45 eV) than $\text{C}_2\text{H}_2\text{O}^+$ (binding energy per atom is 2.90 eV).

We modelled two cations with different chemical composition production possibilities: C_3H_7^+ ($m/z=43$) and $\text{C}_2\text{H}_5\text{N}^+$ ($m/z=43$).

Based on these research results, the appearance energies needed to form $C_3H_7^+$ ($m/z=43$) and $C_2H_5N^+$ ($m/z=43$) agree with the value $E_{ap}=11.85\pm 0.05$ eV measured by (Papp et al., 2012). To determine which fragment is more likely to be produced, we also calculated the binding energy per atom and the HOMO-LUMO gaps of the above-mentioned ions (Table 12).

Table 12. Calculated appearance energy, binding energy per atom and HOMO-LUMO gap values of the cations $C_3H_7^+$ ($m/z=43$) and $C_2H_5N^+$ ($m/z=43$), which might be formed from the fragmentation of the Leu IC conformer in vacuum

Cation $m/z=43$	Appearance energy, eV	Binding energy per atom, eV	HOMO-LUMO gap, eV
$C_3H_7^+$	11.34	3.40	2.24
$C_2H_5N^+$	12.36	3.67	5.11

According to the data (Table 12), the $C_2H_5N^+$ fragment is both thermally and chemically more stable than the $C_3H_7^+$ fragment. Therefore, the $m/z=43$ cation is $C_2H_5N^+$ (complementary anion— $C_4H_8O_2^-$).

We determined that the $m/z=44$ cation is $C_2H_6N^+$. Our established complementary fragment is $C_4H_7O_2^0$. We calculated that the E_{ap} of $C_2H_6N^+$ ($m/z=44$) is 10.16 eV and that the binding energy per atom is 3.60 eV, whereas the E_{ap} of $C_3H_8^+$ ($m/z=44$) is higher (11.18 eV), and its thermal stability is smaller (binding energy per atom is 1.42 eV) than that of $C_2H_6N^+$. The measured $E_{ap}=10.63\pm 0.05$ eV (Papp et al., 2012). Our calculated value (10.16 eV) and the E_{ap} of these authors are in agreement.

The cation at $m/z=57$ could be $C_4H_9^+$ or $C_2H_3NO^+$. We determined that $C_4H_9^+$ ($E_{ap}=10.19$ eV) ion production is more likely than $C_2H_3NO^+$ ($E_{ap}=11.53$ eV) production. Moreover, our calculated value of 10.19 eV and the measured value of 10.65 ± 0.05 eV by (Papp et al., 2012) coincide quite well. Hence, the $m/z=57$ cation was identified as $C_4H_9^+$ (complementary fragment— $C_2H_4NO_2^0$).

The fragment with a mass of $m/z=70$ is $C_5H_{10}^+$, while other ($C_3H_2O_2^+$ and $C_3H_4NO^+$) chemical compositions are less probable; the E_{ap} of these two cations are 10.47 eV and 10.85 eV, respectively. $C_5H_{10}^+$ (complementary fragment— $CH_3NO_2^0$) formation requires an E_{ap} of 9.94 eV. Our obtained appearance energy (9.94 eV) matches the $E_{ap}=9.52\pm 0.05$ eV measured by (Papp et al., 2012).

Based on the obtained results, the peak at mass $m/z=74$ corresponds to $C_2H_4NO_2^+$ (complementary fragment— $C_4H_9^0$). The appearance energy calculated in our research (10.03 eV) coincides with the measured value (10.52 ± 0.05 eV) (Papp et al., 2012).

The positively charged cation at $m/z=75$ has a chemical composition of $C_2H_5NO_2^+$ (complementary fragment— $C_4H_8^0$), and the appearance energy is 9.45 eV. Papp et al. (2012) measured a similar appearance energy of 9.11 ± 0.05 eV.

The most intense peak in the mass spectrum of the Leu positively charged fragment is at $m/z=86$ (NIST, viewed on 2017-03-30). We investigated whether this fragment is $C_5H_{12}N^+$ ($m/z=86$) or $C_3H_4NO_2^+$ ($m/z=86$). Based on our results, producing this fragment would have required 8.93 eV, which is the lowest value among all Leu fragments. The abovementioned research revealed that the cation production requires 9.24 ± 0.05 eV of energy (Papp et al., 2012). Our molecular modelling results show that $C_5H_{12}N^+$ forms after the weakest bond (C5-C6) ruptures (complementary fragment— CO_2H^0).

Our calculated appearance energies required to form cations from the IZ Leu conformer in water are presented in Table 13.

Our theoretical modelling results revealed that the appearance energy needed for the production of cations with the same mass and chemical composition (e.g., the most probable $m/z=86$ ($C_5H_{12}N^+$)) is lower for the decomposition of the L-leucine IC conformer in vacuum than for the fragmentation of the Leu IZ conformer in water.

Table 13. Calculated appearance energies (in eV) of cations formed from the Leu IZ conformer in water

Cation	Complementary fragment	Appearance energy, eV
$C_2H_4^+$ (m/z=28)	$C_4H_9NO_2^-$ (m/z=103)	13.73
$C_2H_5^+$ (m/z=29)	$C_4H_8NO_2^-$ (m/z=102)	13.98
CH_4N^+ (m/z=30)	$C_5H_9O_2^-$ (m/z=101)	11.35
$C_3H_5^+$ (m/z=41)	$C_3H_8NO_2^-$ (m/z=90)	13.58
$C_3H_6^+$ (m/z=42)	$C_3H_7NO_2^0$ (m/z=89)	13.15
$C_2H_5N^+$ (m/z=43)	$C_4H_8O_2^-$ (m/z=88)	13.04
$C_2H_6N^+$ (m/z=44)	$C_4H_7O_2^0$ (m/z=87)	10.74
$C_4H_9^+$ (m/z=57)	$C_2H_4NO_2^0$ (m/z=74)	11.15
$C_5H_{10}^+$ (m/z=70)	$CH_3NO_2^0$ (m/z=61)	10.46
$C_2H_4NO_2^+$ (m/z=74)	$C_4H_9^0$ (m/z=57)	11.13
$C_2H_5NO_2^+$ (m/z=75)	$C_4H_8^0$ (m/z=56)	9.98
$C_5H_{12}N^+$ (m/z=86)	CHO_2^0 (m/z=45)	9.41

Our research also indicates that CH_4N^+ (m/z=30), $C_2H_5N^+$ (m/z=43), $C_2H_6N^+$ (m/z=44), $C_2H_4NO_2^+$ (m/z=74), $C_2H_5NO_2^+$ (m/z=75) and $C_5H_{12}N^+$ (m/z=86) structures are different in different environment. Overall, we found that the positively charged ions that form from the $NH_2-CH(R)-COOH$ structure in vacuum contain NH_2 and $COOH$ groups, while they form from $NH_3^+-CH(R)-COO^-$, with protonated amino and deprotonated carboxyl groups, in water.

2.5. L-isoleucine fragmentation

The most stable conformers of Ile IC (in vacuum) and IZ (in water) are presented in Fig. 5.

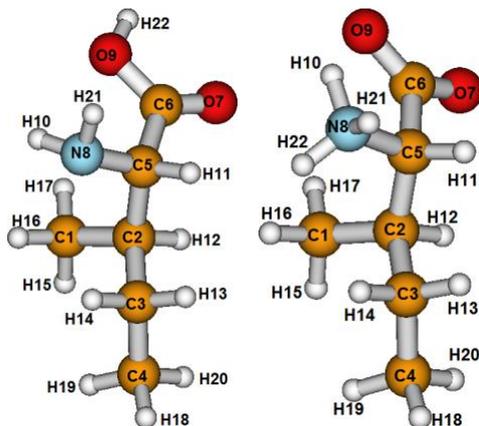


Figure 5. Views of the most stable L-isoleucine conformers. The IC conformer (in vacuum) is on the left, while the IZ conformer (in water) is on the right.

We obtained an IE of 8.34 eV (in vacuum) for the Ile IC conformer (when Ile and its ionized form are in equilibrium), while the Ile IZ IE=9.11 eV. We also established that the weakest bond of Ile IC and IZ is the C5-C6. Another weak bond is C2-C5.

The most prominent peaks are at $m/z=27, 28, 29, 30, 41, 44, 56, 57, 69, 74, 75$ and 86 (NIST, viewed on 2017-12-30) in the Ile cation mass spectrum. In the article by (Papp et al., 2012), it is published that the positively charged fragments at $m/z=42, 43$ and 70 also formed. Below, the calculated appearance energies (in eV) required for the formation of all abovementioned positively charged fragments are presented.

We calculated the total energy, appearance energy, binding energy per atom and HOMO-LUMO gap of $m/z=27$ cations (Table 14).

Table 14. Calculated total energy, appearance energy, binding energy per atom and HOMO-LUMO gap values of cation $C_2H_3^+$ ($m/z=27$), which is formed from the fragmentation of Ile IC

Cation $m/z=27$	Fragment total energy, a.u.	Appearance energy, eV	Binding energy per atom, eV	HOMO-LUMO gap, eV
$C_2H_3^+$ (H_2C-CH^+)	-77.582	12.79	2.67	5.35
$C_2H_3^+$ ($C-CH_3^+$)	-77.508	13.05	2.26	5.54

Our obtained results (Table 14) indicate that the appearance energies of H_2C-CH^+ ($m/z=27$) and $C-CH_3^+$ ($m/z=27$) agree with each other. On the one hand, H_2C-CH^+ ($m/z=27$) is more thermally stable than $C-CH_3^+$. On the other hand, the chemical stabilities of these fragments are the same. Hence, $C-CH_3^+$ could transform to H_2C-CH^+ (whose energy is lower than that of $C-CH_3^+$).

We investigated whether fragments with mass $m/z=28$ are CH_2N^+ or $C_2H_4^+$. The total energy, appearance energy and binding energy per atom of these cations are presented in Table 15.

Table 15. Calculated total energy, appearance energy, and binding energy per atom values of a $C_2H_4^+$ ($m/z=28$) and CH_2N^+ ($m/z=28$) formed from the fragmentation of Ile IC in vacuum

Cation $m/z=28$	Fragment total energy, a.u.	Appearance energy, eV	Binding energy per atom, eV
$C_2H_4^+$	-78.195	12.71	2.72
CH_2N^+ ($HN-CH^+$)	-93.717	11.15	2.86
CH_2N^+ (H_2N-C^+)	-93.636	11.47	2.30

According to our results (Table 15), the lowest appearance energy is needed for CH_2N^+ ($HN-CH^+$) and CH_2N^+ (H_2N-C^+) production (their

E_{ap} values are coincident). However, the E_{ap} values of these cations are above the margin of error compared with the value of 13.93 ± 0.05 eV measured by (Papp et al., 2012). It is noticed that C_2H_4^+ ($m/z=28$) and HN-CH^+ ($m/z=28$) thermal stabilities are similar, i.e., their binding energies per atom are coincident (Table 15). The appearance energy (12.71 eV) needed to produce C_2H_4^+ ($m/z=28$) agrees with the abovementioned experimental value. Hence, the peak at $m/z=28$ was identified as C_2H_4^+ (complementary fragment— $\text{C}_4\text{H}_9\text{NO}_2^-$).

We modelled CH_3N^+ ($m/z=29$) and C_2H_5^+ ($m/z=29$) ion production. The obtained results are presented in Table 16.

Table 16. Calculated appearance energy, binding energy per atom and HOMO-LUMO gap values of the cations C_2H_5^+ ($m/z=29$), CH_3N^+ ($m/z=29$) and CHO^+ ($m/z=29$), which might be formed from the fragmentation of Ile IC

Cation $m/z=29$	Appearance energy, eV	Binding energy per atom, eV	HOMO-LUMO gap, eV
C_2H_5^+	12.45	2.86	8.97
CH_3N^+	12.86	2.59	6.85
CHO^+	13.46	1.16	8.96

Comparing the calculated appearance energy (Table 16) with the $E_{\text{ap}}=12.40 \pm 0.05$ eV measured by (Papp et al., 2012) shows that the appearance energies of C_2H_5^+ ($m/z=29$) and CH_3N^+ ($m/z=29$) are close to the measured values. We also compared other data (Table 16) and noticed that C_2H_5^+ ($m/z=29$) is thermally and chemically more stable than CH_3N^+ . Overall, the C_2H_5^+ ($m/z=29$) ion should dominate (also produced complementary anion $\text{C}_4\text{H}_8\text{NO}_2^-$), but CH_3N^+ ($m/z=29$) could also be produced.

We investigated whether the $m/z=30$ fragment is CH_4N^+ or C_2H_6^+ (Table 17).

Table 17. Calculated appearance energy and binding energy per atom values of cations CH_4N^+ ($m/z=30$) and C_2H_6^+ ($m/z=30$), which might be formed from the fragmentation of the Ile IC conformer in vacuum

Cation $m/z=30$	Appearance energy, eV	Binding energy per atom, eV
CH_4N^+	10.58	2.99
C_2H_6^+	11.24	2.65

It was determined that the cation at $m/z=30$ is CH_4N^+ (complementary fragment— $\text{C}_5\text{H}_9\text{O}_2^0$). This conclusion was made for the following reasons: 1) less energy is needed to produce this fragment than to produce C_2H_6^+ ; 2) its E_{ap} coincides with the measured value (10.24 ± 0.05 eV) (Papp et al., 2012); 3) this fragment is more thermally stable than C_2H_6^+ .

We decided to verify if the peak at $m/z=41$ could be identified as C_3H_5^+ or C_2HO^+ . We obtained that $E_{\text{ap}}(\text{C}_3\text{H}_5^+)=12.49$ eV and $E_{\text{ap}}(\text{C}_2\text{HO}^+)=13.26$ eV. Therefore, less energy is needed to produce C_3H_5^+ ($m/z=41$) than to produce C_2HO^+ ($m/z=41$). Moreover, $E_{\text{ap}}(\text{C}_3\text{H}_5^+)=12.49$ eV coincides with a value of $E_{\text{ap}}=12.61\pm 0.05$ eV measured by (Papp et al., 2012). During the C_3H_5^+ ($m/z=41$) production, a complementary anion ($\text{C}_3\text{H}_8\text{NO}_2^-$) is also produced.

We verify the C_3H_6^+ ($m/z=42$), $\text{C}_2\text{H}_2\text{O}^+$ ($m/z=42$) and $\text{C}_2\text{H}_4\text{N}^+$ ($m/z=42$) ion production probabilities. We determined that C_3H_6^+ ($m/z=42$) production requires the smallest E_{ap} (11.87 eV) and that this value is in agreement with the ($E_{\text{ap}}=12.45\pm 0.05$ eV) measured by (Papp et al., 2012). In contrast, $E_{\text{ap}}(\text{C}_2\text{H}_2\text{O}^+)=13.09$ eV and $E_{\text{ap}}(\text{C}_2\text{H}_4\text{N}^+)=13.46$ eV. Hence, the $m/z=42$ cation is C_3H_6^+ (complementary fragment— $\text{C}_3\text{H}_7\text{NO}_2^-$).

C_3H_7^+ ($m/z=43$) and $\text{C}_2\text{H}_5\text{N}^+$ ($m/z=43$) cation production from Ile due to low-energy electrons was investigated. The main data (appearance energy, binding energy per atom and HOMO-LUMO gap values) are presented in Table 18.

Table 18. Calculated appearance energy, binding energy per atom and HOMO-LUMO gap values of cations $C_3H_7^+$ ($m/z=43$) and $C_2H_5N^+$ ($m/z=43$), which might be formed from fragmentation of the Ile IC conformer in vacuum

Cation $m/z=43$	Appearance energy, eV	Binding energy per atom, eV	HOMO-LUMO gap, eV
$C_3H_7^+$	12.29	3.47	7.24
$C_2H_5N^+$	11.56	3.57	6.37

The E_{ap} is lower for $C_2H_5N^+$ ($m/z=43$) than for $C_3H_7^+$ ($m/z=43$). The binding energy per atom of these fragments is similar (Table 18); hence, their thermal stabilities are the same. In contrast, the appearance energy (12.29 eV) of $C_3H_7^+$ ($m/z=43$) is closer to the experimentally measured value (12.70 ± 0.05 eV) (Papp et al., 2012). In addition, $C_3H_7^+$ ($m/z=43$) is more chemically stable than $C_2H_5N^+$ ($m/z=43$). Our molecular modelling results indicate that $C_3H_7^+$ ($m/z=43$) is the dominant cation among the $m/z=43$ fragments. During this process, $C_3H_6NO_2^-$ (complementary anion) was also produced.

During molecular modelling, we determined that the peak at $m/z=44$ (NIST, viewed on 2017-12-30) could be identified as $C_2H_6N^+$ (complementary ion— $C_4H_7O_2^-$). The appearance energy needed to form $C_2H_6N^+$ (11.46 eV) coincides with the measured value of $E_{ap}=11.09\pm 0.05$ eV (Papp et al., 2012). In contrast, more energy is needed to produce $C_3H_8^+$ ($m/z=44$) (11.93 eV) than to produce $C_2H_6N^+$, and the energy of the latter is outside the error margin. Moreover, $C_2H_6N^+$ ($m/z=44$) is more chemically stable than $C_3H_8^+$ (Table 19).

Table 19. Calculated appearance energy of cations $C_2H_6N^+$ ($m/z=44$) and $C_3H_8^+$ ($m/z=44$) formed from the fragmentation of Ile IC conformers in vacuum along with binding energy per atom values

Cation $m/z=44$	Appearance energy, eV	Binding energy per atom, eV
$C_2H_6N^+$	11.46	4.63
$C_3H_8^+$	11.93	3.23

We calculated the $C_3H_6N^+$ ($m/z=56$) and $C_2H_2NO^+$ ($m/z=56$) fragment appearance energy, binding energy per atom and HOMO-LUMO gap (Table 20).

Table 20. Calculated total energy, appearance energy, binding energy per atom and HOMO-LUMO gap values of cations $C_3H_6N^+$ ($m/z=56$) and $C_2H_2NO^+$ ($m/z=56$) formed from the fragmentation of the Ile IC conformer in vacuum

Cation $m/z=56$	Fragment total energy, a.u.	Appearance energy, eV	Binding energy per atom, eV	HOMO-LUMO gap, eV
$C_3H_6N^+$ ($H_2N-CH-C-CH_3^+$)	-172.303	13.14	3.84	3.15
$C_3H_6N^+$ ($H_2N-CH-CH-CH_2^+$)	-172.378	13.24	4.05	5.22
$C_2H_2NO^+$	-207.047	13.96	3.93	3.63

$C_3H_6N^+$ ($H_2N-CH-C-CH_3^+$ and $H_2N-CH-CH-CH_2^+$) production requires less energy than $C_2H_2NO^+$ production (Table 20). Our results revealed that $H_2N-CH-CH-CH_2^+$ is thermally and chemically more stable than $H_2N-CH-C-CH_3^+$. Therefore, $H_2N-CH-CH-CH_2^+$ is dominant. During the production of this positively charged ion, $C_3H_7O_2^-$ (the complementary anion) also forms.

We investigated which of the chemical composition $C_4H_9^+$, $C_3H_7N^+$, $C_2H_3NO^+$ and $C_2HO_2^+$ corresponds to the peak at $m/z=57$ (Table 21).

We noted that the E_{ap} of $C_4H_9^+$ ($m/z=57$), $C_3H_7N^+$ ($m/z=57$) and $C_2H_3NO^+$ ($m/z=57$) (Table 21) coincide with the experimental value (10.64 ± 0.05 eV) measured by (Papp et al., 2012). The thermal stabilities of these three cations are similar, while $C_2H_3NO^+$ ($m/z=57$) is the most chemically stable among them. Therefore, $C_2H_3NO^+$ (complementary fragment— $C_4H_6O_2^-$) is the most likely of these cations to be produced during Ile fragmentation, but $C_4H_9^+$ ($m/z=57$) and $C_3H_7N^+$ ($m/z=57$) could also form.

Table 21. Calculated appearance energy, binding energy per atom and HOMO-LUMO gap values of $C_4H_9^+$ ($m/z=57$), $C_3H_7N^+$ ($m/z=57$), $C_2H_3NO^+$ ($m/z=57$) and $C_2HO_2^+$ ($m/z=57$) formed from the fragmentation of Ile IC conformer in vacuum

Cation $m/z=57$	Appearance energy, eV	Binding energy per atom, eV	HOMO-LUMO gap, eV
$C_4H_9^+$	10.16	3.73	5.68
$C_3H_7N^+$	10.40	3.68	5.17
$C_2H_3NO^+$	10.59	3.91	6.38
$C_2HO_2^+$	11.26	2.94	4.64

The positively charged ion at $m/z=69$ could be $C_5H_9^+$, $C_4H_5O^+$ or $C_4H_7N^+$. Our calculated E_{ap} values of these cations, binding energies per atom and HOMO-LUMO gaps are presented in Table 22.

Table 22. Calculated appearance energy, binding energy per atom and HOMO-LUMO gap values of $C_5H_9^+$ ($m/z=69$), $C_4H_5O^+$ ($m/z=69$) and $C_4H_7N^+$ ($m/z=69$), which might be formed from the fragmentation of the Ile IC conformer in vacuum

Cation $m/z=69$	Appearance energy, eV	Binding energy per atom, eV	HOMO-LUMO gap, eV
$C_5H_9^+$	11.21	3.94	2.59
$C_4H_5O^+$	11.72	4.30	5.78
$C_4H_7N^+$	11.59	4.16	4.54

We established that the appearance energy of all mentioned fragments coincided with the measured value of 11.41 ± 0.05 eV (Papp et al., 2012). Based on our results (Table 22), $C_4H_5O^+$ ($m/z=69$) and $C_4H_7N^+$ ($m/z=69$) are the most thermally stable of these cations, while $C_4H_5O^+$ ($m/z=69$) is the most chemically stable. Hence, the $m/z=69$ cation could be identified as either $C_4H_5O^+$ or $C_4H_7N^+$, but $C_4H_5O^+$ is more likely. During $C_4H_5O^+$ ($m/z=69$) production, $C_2H_8NO^-$ (the complementary fragment) was also produced.

We studied whether $m/z=70$ represented $C_5H_{10}^+$ or $C_4H_8N^+$. We determined that the lowest appearance energy (9.49 eV) is needed to form $C_5H_{10}^+$ ($m/z=70$). On the other hand, the E_{ap} of 10.86 eV required to form $C_4H_8N^+$ ($m/z=70$) is closer to the value of 11.36 ± 0.05 eV measured by (Papp et al., 2012). Hence, both cations could be produced, but $C_4H_8N^+$ ($m/z=70$) should be the dominant form.

We established that the peak at $m/z=74$ corresponds to $C_2H_4NO_2^+$ which forms when the L-isoleucine side chain ($C_4H_9^0$) dissociates. The energy needed to form this cation is 9.86 eV. The appearance energy (9.86 eV) coincides with that measured by (Papp et al., 2012) (10.29 ± 0.05 eV).

We also determined that the $m/z=75$ ion is $C_2H_5NO_2^+$. The formation of $C_2H_5NO_2^+$ involves complementary fragment $C_4H_8^0$ formation. The E_{ap} that we calculated (9.48 eV) coincides with the value of 9.71 ± 0.05 eV measured by (Papp et al., 2012).

We analysed whether the peak at $m/z=86$ corresponds to $C_5H_{12}N^+$ or $C_3H_4NO_2^+$. According to our results, $C_5H_{12}N^+$ ($m/z=86$) production requires 8.74 eV, while $C_3H_4NO_2^+$ ($m/z=86$) production requires 9.58 eV. The calculated E_{ap} (8.74 eV) coincides with the E_{ap} (9.11 ± 0.05 eV) measured by (Papp et al., 2012). Based on our results, production of the $C_5H_{12}N^+$ ($m/z=86$) is the most likely during Ile fragmentation. Our molecular modelling results indicate that this cation forms after the weakest (C5-C6) bond ruptures, i.e., after dissociation of the neutral carboxyl group.

The E_{ap} values needed to form cations from the Ile IZ conformer in water are presented in Table 23.

Similar to Thr, Gln and Leu fragmentation, the energy needed for the production of positively charged fragments with the same mass and chemical composition is lower for the decomposition of the L-isoleucine IC conformer in vacuum than for the fragmentation of the Ile IZ conformer in water.

Table 23. Calculated appearance energies (in eV) of cations formed from the Ile IZ conformer in water

Cation	Complementary fragment	Appearance energy, eV
$C_2H_3^+$ (m/z=27)	$C_4H_{10}NO_2^-$ (m/z=104)	14.05
$C_2H_4^+$ (m/z=28)	$C_4H_9NO_2^-$ (m/z=103)	13.53
$C_2H_5^+$ (m/z=29)	$C_4H_8NO_2^-$ (m/z=102)	13.12
CH_4N^+ (m/z=30)	$C_5H_9O_2^0$ (m/z=101)	11.29
$C_3H_5^+$ (m/z=41)	$C_3H_8NO_2^-$ (m/z=90)	13.34
$C_3H_6^+$ (m/z=42)	$C_3H_6^+$ (m/z=42)	12.48
$C_3H_7^+$ (m/z=43)	$C_3H_6NO_2^-$ (m/z=88)	13.05
$C_2H_6N^+$ (m/z=44)	$C_4H_7O_2^-$ (m/z=87)	12.24
$C_3H_6N^+$ (m/z=56)	$C_3H_7O_2^-$ (m/z=75)	13.99
$C_2H_3NO^+$ (m/z=57)	$C_4H_6O_2^-$ (m/z=74)	11.47
$C_4H_5O^+$ (m/z=69)	$C_2H_8NO^-$ (m/z=62)	12.37
$C_4H_8N^+$ (m/z=70)	$C_2H_5O_2^0$ (m/z=61)	11.47
$C_2H_4NO_2^+$ (m/z=74)	$C_4H_9^0$ (m/z=57)	11.15
$C_2H_5NO_2^+$ (m/z=75)	$C_4H_8^0$ (m/z=56)	10.08
$C_5H_{12}N^+$ (m/z=86)	CHO_2^0 (m/z=45)	9.58

Our results reveal that CH_4N^+ ($m/z=30$), $\text{C}_2\text{H}_6\text{N}^+$ ($m/z=44$), $\text{C}_3\text{H}_6\text{N}^+$ ($m/z=56$), $\text{C}_2\text{H}_4\text{NO}_2^+$ ($m/z=74$), $\text{C}_2\text{H}_5\text{NO}_2^+$ ($m/z=75$) and $\text{C}_5\text{H}_{12}\text{N}^+$ ($m/z=86$) structures are different in different environment. We noted that H atom migration between amino and carboxyl groups does not occur, i.e., the abovementioned fragments have NH_2 and COOH groups when they form from the $\text{NH}_2\text{-CH(R)-COOH}$ structure in vacuum and have NH_3^+ and COO^- groups, when they form from the $\text{NH}_3^+\text{-CH(R)-COO}^-$ structure in water.

2.6. Comparison of L-glutamic acid and L-glutamine fragmentation

The masses of L-glutamic acid and L-glutamine are similar (147 Da and 146 Da, respectively). During the fragmentation of these AAs, cations with the same masses ($m/z=28, 41, 56, 84$) are produced. However, the side chains of these AAs are very different: Glu has a $-(\text{CH}_2)_2\text{-COOH}$ side chain, while Gln has a $-(\text{CH}_2)_2\text{-CO(NH}_2)$ side chain. Three of four of the cations with the same mass have different chemical compositions, and they were produced during Glu and Gln fragmentation. Neutral Glu molecules could split into fragments only in vacuum. However, Glu charge is negative in water. Due to the negative charge, Glu could not be fragmented by low-energy electrons. Gln, whose canonical and zwitterionic forms are neutral, could undergo fragmentation both in vacuum and water.

2.7. Comparison of L-leucine and L-isoleucine fragmentation

Most cations produced during Leu and Ile fragmentation have the same mass and chemical compositions. The reasons for this phenomenon are 1) that Leu and Ile have the same mass (131 Da) and 2) that the weakest bond in these AAs is the same. We also noticed that the appearance energies of most of the fragments with the same mass and chemical composition are approximately equal. However, their

different methyl group positioning could be the reason why 1) several of the cations with the same mass that are formed during Leu and Ile fragmentation have different chemical compositions and 2) the appearance energies required to form the several same cations differ by more than the statistical error margin. In addition, we determined that $C_4H_5O^+/C_4H_7N^+$ ($m/z=69$) could be produced only during Ile fragmentation. Hence, the peak at $m/z=69$ could be a diagnostic peak specific for Ile. These data are very useful for separating Leu and Ile AAs in protein sequencing experiments. The diagnostic peak at this mass is also observed in the cation mass spectra of Ile (NIST, viewed on 2017-12-30).

2.8. L-threonine, L-glutamine, L-leucine and L-isoleucine fragmentation in water

As mentioned above, we established that the production of the same fragments (same mass and chemical composition) requires more energy in water than in vacuum. It was assumed that AA fragmentation in water requires more energy than that in vacuum because intermolecular bonds between AAs and water must be cleaved. The PCM does not accurately describe the formation of hydrogen bonds between biomolecules and the solution in all cases. To check the validity of this assumption, we performed additional research. First, we determined the most stable Thr-H₂O, Gln-H₂O, Leu-H₂O, and Ile-H₂O complexes (Fig. 6).

Then, we calculated the most likely fragment appearance energies (Table 24) for cations formed during complex (Fig. 6) fragmentation. The obtained appearance energies were compared with the energies needed to form the same fragments; then, AA fragmentation was observed in water although Thr (Fig. 1), Gln (Fig. 3), Leu (Fig. 4), and Ile (Fig. 5) do not form bonds with water molecules.

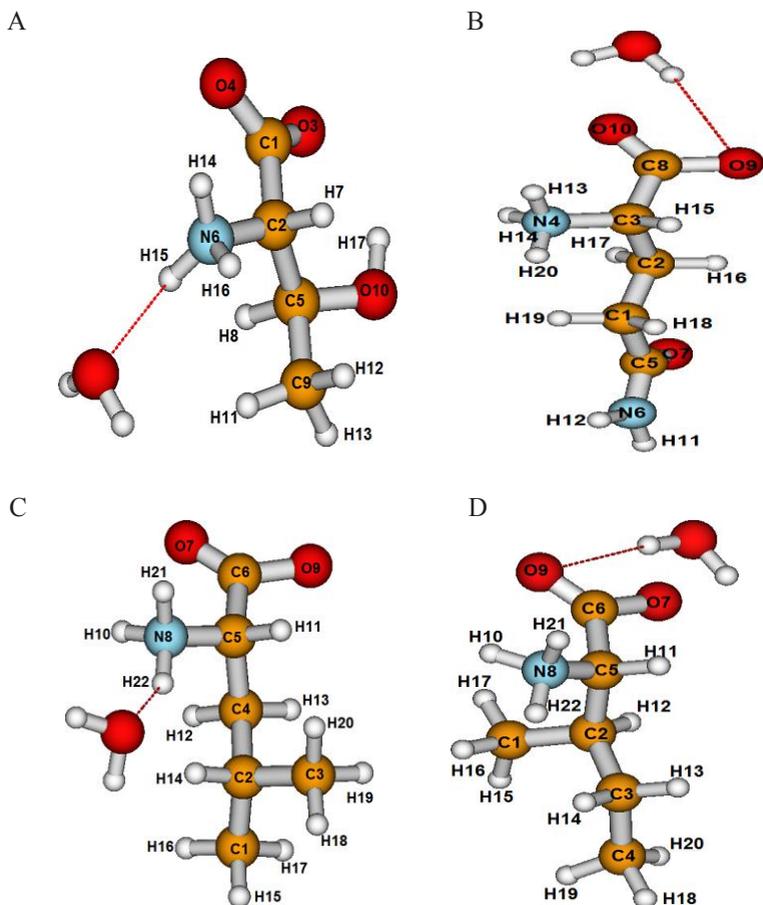


Figure 6. Views of the most stable amino acid complexes in water: A—L-threonine IZ-H₂O, B—L-glutamine IZ-H₂O, C—L-leucine IZ-H₂O and D—L-isoleucine IZ-H₂O.

Based on our results (Tables 4, 8, 13, 23 and 24), more energy is needed to produce the same fragments from L-threonine IZ-H₂O, L-glutamine IZ-H₂O, L-leucine IZ-H₂O and L-isoleucine IZ-H₂O complexes than from the corresponding AAs not in complexes with water. Overall, the obtained results revealed that the production of the cations requires more energy in water than in vacuum due to the intermolecular hydrogen bonds between AAs and water molecules.

Table 24. Calculated appearance energy (in eV) of $C_3H_9NO^+$ ($m/z=75$), $C_4H_8N_2^+$ ($m/z=84$) and $C_5H_{12}N^+$ ($m/z=86$) formed from L-threonine IZ-Allo- H_2O , L-glutamine IZ- H_2O , L-leucine IZ- H_2O and L-isoleucine IZ- H_2O complexes, respectively, in water

Complex	L-threonine IZ-H_2O	L-glutamine IZ-H_2O	L-leucine IZ-H_2O	L-isoleucine IZ-H_2O
Fragment	$C_3H_9NO^+$ ($m/z=75$)	$C_4H_8N_2^+$ ($m/z=84$)	$C_5H_{12}N^+$ ($m/z=86$)	$C_5H_{12}N^+$ ($m/z=86$)
E_{ap} , eV	9.73	9.88	10.01	10.06

CONCLUSIONS

We determined the most stable conformers of L-threonine, L-glutamic acid, L-glutamine, L-leucine and L-isoleucine in vacuum and water. The results indicated the following:

1. The production of positively charged fragments with the same mass and chemical composition in water required more appearance energy than that in vacuum.
2. The results of this study indicate that the structures of fragments with the same mass and chemical composition depend on the environment.
3. L-glutamic acid and L-glutamine, with a similar mass (a difference of 1 Da) but different chemical compositions, undergo fragmentation by low-energy in a similar manner;
4. L-leucine and L-isoleucine, with the same mass and chemical composition but different geometrical structures, undergo fragmentation by low-energy in a similar manner.

REFERENCES

- [1] UNSCEAR. United Nations Scientific Committee on the Effects of Atomic Radiation. Sources and effects of ionizing radiation. Report to the General Assembly, with Scientific Annexes. United Nations, New York. 2000.
- [2] Brenner DJ & Hall EJ (2007). Computed tomography—an increasing source of radiation exposure. *N Engl J Med* **357**(22), 2277-2284.
- [3] de Hoffmann E & Stroobant V (2007). *Mass Spectrometry Principles and Applications*. 3th edition. England. John Wiley & Sons, Ltd.
- [4] Boudaïffa B, Cloutier P, Hunting D, Huels MA & Sanche L (2000). Resonant formation of DNA strand breaks by low-energy (3 to 20 eV) electrons. *Science* **5458**(287), 1658-1660.
- [5] Barrios R, Skurski P, and Simons J (2002). Mechanism for damage to DNA by low-energy electrons. *J Phys Chem B* **106**(33), 7991–7994.
- [6] Huels MA, Boudaïffa B, Cloutier P, Hunting D, & Sanche L (2003). Single, Double, and Multiple Double Strand Breaks Induced in DNA by 3–100 eV Electrons. *J Am Chem Soc* **125**(15), 4467- 4477.
- [7] Tonzani S & Greene CH (2006). Low-energy electron scattering from DNA and RNA bases: Shape resonances and radiation damage. *J Chem Phys* **124**(5), 1–43.
- [8] Ipolyi I, Cicman P, Denifl S, Matejčík V, Mach P, Urban J, Scheier P., Märk TD & Matejčík Š (2006). Electron impact ionization of alanine: Appearance energies of the ions. *Int J Mass Spectrom* **252**(3), 228-233.
- [9] Tamuliene J, Romanova L, Vukstich V, Papp A, Shkurin S, Baliulyte L & Snegursky A (2016). On the influence of low-energy ionizing radiation on the amino acid molecule: proline. *Eur Phys J D* **70**(6),143.
- [10] Farajmand B and Bahrami H (2016). Electron ionization of

serine and threonine: A Discussion about Peak Intensities. *Phys Chem Res* **4**(4),539-551.

- [11] Walsh NP, Blannin AK, Robson PJ & Gleeson M (1999). Glutamine, exercise and immune function: Links and possible mechanisms. *Sport Med* **26**(3),177–191.
- [12] Li P, Yin YL, Li D, Kim SW & Wu G (2007). Amino acids and immune function. *Br J Nutr* **98**(2), 237.
- [13] Wu G (2009). Amino acids: metabolism, functions, and nutrition. *Amino Acids* **37**(1), 1—17.
- [14] Wu G (2013). Functional amino acids in nutrition and health. *Amino Acids* **45**(3), 407–411.
- [15] Gordon M (2013). *Pigment Cell Growth: Proceedings of the Third Conference on the Biology of Normal and Atypical Pigment Cell Growth*. New York. Academic Press.
- [16] Forshier S (2009). *Essentials of radiation biology and protection*. 2nd edition. New York, NY: Delmar, Cengage Learning.
- [17] Palsson BØ (2011). *Systems Biology: Simulation of Dynamic Network States*. 1st edition. United Kingdom, Cambridge University Press.
- [18] Tamminen S, Webster A, Vermeulen N (2013). *Bio-objects– Life in the 21st Century*. United Kingdom, Ashgate Publishing.
- [19] Alberts B, Bray D, Hopkin K, Johnson AD, Lewis J, Raff M, Roberts K & Walter P (2014). *Essential Cell Biology*. 4th edition. United States of America, Garland Science.
- [20] Roddick-Lanzilotta AD and McQuillan AJ (2000). An in situ infrared spectroscopic study of glutamic acid and of aspartic acid adsorbed on TiO₂: Implications for the biocompatibility of titanium. *J Colloid Interface Sci* **227**(1), 48–54.
- [21] Latha MP, Rao VM, Rao TS & Rao GN (2007). Determination of protonation constants of L-glutamic acid and L-methionine in 1,2-propanediol-water mixtures. *Acta Chim Slov* **54**(1), 160–165.
- [22] Leela AC, Rani RS, and Rao GN (2012). Solvent effect on protonation equilibria of L-aspartic acid and ethylenediamine in dioxan-water mixtures. *Proc Natl Acad Sci India Sect A - Phys Sci* **82**(3), 197–204.

- [23] Roddick-Lanzilotta AD, Connor PA, & McQuillan AJ (1998). An in situ infrared spectroscopic study of the adsorption of lysine to TiO_2 from an aqueous solution. *Langmuir* **14**(22), 6479–6484.
- [24] Kuvaeva ZI, Koval'Chuk IV, Vodop'Yanova LA & Soldatov S (2013). Phase equilibria in a system of aqueous arginine with an octane solution of sulfonic acid. *Russ J Phys Chem A* **87**(5), 772–776.
- [25] Raju S, Naik KBK, Kumar BA & Rao GN (2016). Protonation Equilibria Of L-Glutamic Acid And L-Histidine In Low Dielectric Media. *Glob res dev j eng* **2**(1), 11–17.
- [26] Ren Y & Kresin VV (2008). Suppressing the fragmentation of fragile molecules in helium nanodroplets by coembedding with water: Possible role of the electric dipole moment. *J Chem Phys* **128**(7), 1–9.
- [27] Ren Y, Moro R & Kresin VV (2007). Changing the fragmentation pattern of molecules in helium nanodroplets by co-embedding with water. *Eur Phys J D* **43**(1–3), 109–112.
- [28] Denifl S, Mähr I, da Silva FF, Zappa F, Märk TD & Scheier P (2009). Electron impact ionization studies with the amino acid valine in the gas phase and (hydrated) in helium droplets. *Eur Phys J D* **51**(1), 73–79.
- [29] Armirotti A, Millo E & Damonte G (2007). How to Discriminate Between Leucine and Isoleucine by Low Energy ESI-TRAP MSn. *J Am Soc Mass Spectrom* **18**(1), 57–63.
- [30] Bagal D, Kast E & Cao P (2017). Rapid Distinction of Leucine and Isoleucine in Monoclonal Antibodies Using Nanoflow LCMSn. *Anal Chem* **89**(1), 720–727.
- [31] Nalivaeva NN & Turner AJ (2001). Post-translational modifications of proteins: Acetylcholinesterase as a model system. *Proteomics* **1**(6), 735–747.
- [32] Tamuliene J, Romanova L, Vukstich V, Papp A, Baliulyte L & Snegursky A (2018). On the influence of low-energy ionizing radiation on the amino acid molecule: Valine case. *Lith J Phys* **58**(2).
- [33] Tamuliene J, Romanova LG, Vukstich VS, Papp AV & Snegursky AV (2015). Electron-impact-induced tryptophan molecule fragmentation. *Eur Phys J D* **69**(1).

- [34] Tamuliene J, Romanova LG, Vukstich VS, Papp AV & Snegursky AV (2014). Electron-impact-induced asparagine molecule fragmentation. *Eur Phys J D* **68**(5), 118.
- [35] Mulliken RS (1955). Electronic population analysis on LCAO–MO molecular wave functions. I. *J Chem Phys* **23**(10), 1833–1840.
- [36] Young DC (2001). *Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems*. United States of America. John Wiley & Sons.
- [37] Smalo HS, Astrand PO & Ingebrigtsen S (2010). Calculation of ionization potentials and electron affinities for molecules relevant for streamer initiation and propagation. *IEEE Trans Dielectr Electr Insul* **17**(3), 733–741.
- [38] National Institute of Standards, Standard Reference Database: Chemistry Webbook. <http://webbook.nist.gov/chemistry/>.
- [39] Skyner RE, McDonagh JL, Groom CR, Van Mourik T & Mitchell JBO. (2015). A review of methods for the calculation of solution free energies and the modelling of systems in solution. *Phys Chem Chem Phys* **17**(9), 6174–6191.
- [40] Frisch MJ et al. (2004) GAUSSIAN 03, Revision D.02, Gaussian Inc., Wallingford, CT.
- [41] Frisch MJ et al. (2016) GAUSSIAN 09, Revision D.02, Gaussian, Inc. Wallingford CT.
- [42] Schaftenaar G & Noordik JH (2000). Molden: a pre-and post-processing program for molecular and electronic structures. *J Comput Aid Mol Des* **14**(2), 123–134.
- [43] Tamuliene J, Romanova L, Vukstich V, Papp A, Baliulyte L & Snegursky A (2019). The impact of low-energy ionizing radiation on glutamine. *Int J Mass Spectrom* **444**, 116185.
- [44] Cannington PH & Ham NS (1979). The photoelectron spectra of amino-acids: A survey. *J Electron Spectrosc* **15**(1), 79–82.
- [45] Papp P, Shchukin P, Kočíšek J & Š Matejčík Š (2012). Electron ionization and dissociation of aliphatic amino acids. *J Chem Phys* **137**(10), 105101, 1–9.

LIST OF PUBLICATIONS

Publications resulting the dissertation

Journal papers

1. Tamuliene J., Romanova L., Vukstich V., Papp A., **Baliulyte L.**, Snegursky A. The impact of low-energy ionizing radiation on glutamine. *International Journal of Mass Spectrometry* 2019; 444.
2. **Baliulyte L.**, Tamuliene J., On the influence of water on fragmentation of the amino acid L-threonine. *Open physics* 2019; 17(1):250-262.

Conference materials

Article in the non-peer-reviewed foreign international conference proceedings

1. **Baliulyte L.**, Tamuliene J. In silico of the influence of water on the L-leucine and L-isoleucine molecules fragmentation. EP-2019 International Conference of young scientists and post-graduates, 2019 05 21-24; Uzhhorod, Ukraine.

Conference abstracts in the non-peer-reviewed publications

1. **Baliulyte L.**, Tamuliene J. In silico study of L-glutamic acid and L-glutamine fragmentation by low energy electrons 63rd international conference for students of physics and natural sciences Open Readings 2020; 2020 03 17-20; Vilnius, Lietuva.
2. **Baliulyte L.**, Tamuliene J. A study on the influence of water on the L-leucine fragmentation. 62th Scientific Conference for Young Students of Physics and Natural Science Open Readings 2019; 2019 03 19-22; Vilnius, Lithuania.
3. **Baliulyte L.**, Tamuliene J. In silico of the influence of water on the L-isoleucine molecule fragmentation. Baltic biophysics conference 2018; 2018 10 04-05, Kaunas, Lithuania.
4. **Baliulyte L.**, Tamuliene J. Water influence on L-glutamic acid fragmentation. 8-th young research conference Interdisciplinary

research in the physical and technological sciences 2018; 2018 02 08, Vilnius, Lithuania.

5. **Baliulyte L.**, Tamuliene J. Ab initio study of water influence on L-threonine fragmentation. 42nd Lithuanian National Conference on Physics 2017; 2017 10 04-06, Vilnius, Lithuania.
6. Snegursky A.V. Tamuliene J., Romanova L.G., Vukstich V.S., Papp A.V., **Baliulyte L.**, Snegurskaya T.A. On the influence of low-energy ionizing radiation on the amino acid molecule: glutamine. 4th General Meeting COST Action CM1204, 2017 03 14-16; Prague, Czech Republic.
7. **Baliulyte L.**, Tamuliene J. Theoretical study of threonine molecule fragmentation by low energy electrons. Fourth International Conference on Radiation and Applications in Various Fields of Research (RAD 2016); 2016 05 23-27; Niš, Serbia.
8. **Baliulyte L.**, Tamuliene J. Study of threonine fragmentation by low energy electrons. 6-th young research conference. Interdisciplinary research in the physical and technological sciences 2016; 2016 02 10; Vilnius, Lithuania.
9. **Baliulyte L.**, Tamuliene J. Threonine fragmentation by low energy electrons. International conference Vita Scientia 2016; 2016 01 04; Vilnius, Lithuania.

Abstracts in other peer-reviewed publications

1. Demes S., Tamuliene J., **Baliulyte L.**, Romanova L., Vukstich V., Papp A. and Snegursky A. Fragmentation of Glutamine Molecule by Low-Energy Electron-Impact. XX International workshop on Low-Energy Positron and Positronium Physics, XXI International Symposium on Electron-Molecule Collisions and Swarms, V Workshop on Non-Equilibrium Processes, 2019 07 18-21; Belgrade, Serbia.
2. **Baliulyte L.**, Tamuliene J. In silico of the influence of water on the L-leucine molecule. FEBS3+ conference of Latvian, Lithuanian and Estonian biochemical societies 2019; 2019 06 17-19; Riga, Latvian. 3. **Baliulyte L.**, Tamuliene J. A study on the influence of water on the L-glutamic acid fragmentation. 7th International Conference Aspects of Neuroscience 2017; 2017 11 24-26; Warsaw, Poland.

Theses in the international databases

1. **Baliulyte L.**, Tamuliene J. A study on the influence of water on the L-isoleucine fragmentation. Journal of analytical & bioanalytical techniques, vol. 9.2018.

Conference presentation

1. **Baliulyte L.**, Tamuliene J. A study on the influence of water on the L-leucine fragmentation. 4th Life sciences baltics 2018; 2018 09 26-27; Vilnius, Lithuania.

Other publications (on the subject
which are not included in the dissertation)

Journal papers

1. Tamuliene J., Romanova L., Vukstich V., Papp A., **Baliulyte L.**, Snegursky A., On the influence of low-energy ionizing radiation on the amino acid molecule: valine. Lithuanian Journal of Physics 2018; 58(2).
2. Tamuliene, J., Romanova, L., Vukstich, V., Papp, A., Shkurin, S., **Baliulyte, L.**, & Snegursky, A. On the influence of low-energy ionizing radiation on the amino acid molecule: proline. The European Physical Journal D 2016; 70(6):1-10.

Peer-reviewed extended abstracts

1. Papp P., Vukstich V, Romanova L., Tamuliene J., **Baliulyte L.**, Snegursky A. Mass-spectrometric studies of the valine molecule fragmentation by electron impact. ECAMP 12: 12th European Conference on Atoms Molecules and Photons, 2016 10 05-09; Frankfurt am Main, Germany.

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