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ELECTRON-IMPACT IONIZATION OF TYROSINE AND THREONINE AMINO ACID MOLECULES

For a tyrosine amino acid molecule, the energy dependence of the electron-impact single-ionization cross-section is measured, and its threshold is determined. By normalizing the experimental relative cross-section values by the theoretical ones, the absolute cross-section values are determined. The ionization potentials of tyrosine and threonine molecules are evaluated theoretically on the basis of the binding energies of their highest occupied orbitals. The characteristics of molecular orbitals are calculated using the Hartree–Fock and density functional theory methods. The cross-sections of the single-ionization of the D- and L-forms of examined molecules are evaluated in the framework of the Binary–Encounter–Bethe model and using the Gryzinski formula.

K e y w o r d s: amino acid, ionization potential, molecular orbital, ionization cross-section.

1. Introduction

The study of the processes that take place at the collisions of low-energy electrons with biomolecules is one of the main directions in modern sciences such as physics, chemistry, and biology. Those processes make it possible to obtain the important information: the binding, dissociation, excitation, and ionization energies of target molecules, as well as the excitation and ionization potentials in the excitation, ionization, and dissociative ionization reactions. In this regard, important are integral and differential parameters of the indicated processes, in particular, the cross-sections of elastic scattering (elastic, viscous, and momentum transfer ones), excitation, and ionization [1].

Amino acids are basic structural units of proteins. They contain the amino (-NH_2) and carboxyl (-COOH) groups. They are classified as acidic, basic, and neutral. Some of them are called essential (e.g., threonine), because they are not synthesized in the human organism or are synthesized in insufficient amounts, so they must be taken with food. Other amino acids can be synthesized in the organism; they are called nonessential (e.g., tyrosine). Some amino acids are synthesized in the organism, but their yield is insufficient, so they are classified as semiessential.

When interacting with electrons possessing a high (thermal) or low (a few tens of eVs) collision energy, molecules can dissociate (decay into fragments). At low collision energies, these are processes of dissociative electron attachment (capture); at high energies, these are dissociative processes of electron-impact molecular excitation and ionization.

The study of the physicochemical processes occurring at the interaction of various biomolecules with high- or low-energy electrons is a challenging task in recent years [2–5]. Here, very important are biophysical and biochemical consequences induced by those processes in the molecule structure and the organism cells.

In work [2], the absolute values of the total and partial electron-impact ionization cross-sections were

measured for such important biomolecules as adenine and guanine at energies from the corresponding thresholds to 200 eV. In work [3], the fragmentation of the glutamine and glutamic acid molecules in the gas phase by the electron impact was experimentally studied, and their ionization potentials were measured. In the theoretical work [4], the structural parameters for the threonine and glutamine amino acids, glutamic acid, leucine, and isoleucine were calculated. In work [5], single-ionization cross-sections were calculated for the uracil, thymine, cytosine, adenine, and guanine biomolecules, which are components of nucleic acids. In a series of experimental works (see, for example, works [6–8]), the mass spectra obtained at the fragmentation of such amino acids as glycine, methionine, asparagine, tryptophan, proline, alanine, valine, and glutamine were systematically analyzed. In recent works [9, 10], the fragmentation dynamics in the process of dissociative ionization of the threonine and tyrosine amino acid molecules by the electron impact was studied experimentally and theoretically, and the appearance energies for some fragment ions were determined.

In this work, the single-ionization of the tyrosine ($C_9H_{11}NO_3$) and threonine ($C_4H_9NO_3$) molecules was studied experimentally and theoretically. Tyrosine is one of 20 standard amino acids used by cells to synthesize proteins. Tyrosine degradation products can change the physical and chemical properties of proteins and, as a result, provoke various diseases. On the other hand, tyrosine plays an important role in charge transfer processes in biological systems. These processes can also be disturbed owing to the degradation of this amino acid. The regulation of cellular functioning in a large variety of diseases, including cancer, can be violated because of tyrosine degradation, since receptor protein-tyrosine kinases are involved in this regulation.

Threonine also belongs to 20 standard amino acids. Being an essential amino acid, it is not synthesized in the human organism and must be included in the dietary intake. Threonine provides the normal functioning of the human organism, in particular, the functioning of the immune, central nervous, and cardiovascular systems. It participates in the production of collagen, muscle tissue, and elastin.

In this work, theoretical calculations of the single-ionization cross-sections of the D- and L-forms of the tyrosine and threonine molecules were carried out in the framework of the Binary–Encounter–Bethe model and using the Gryzinsky formula (see also work [5]). We took the parameters of molecular orbitals (MOs) calculated using the Hartree–Fock (HF) method and the aug-cc-pTVZ basis set, and following the density-functional-theory (DFT) methods. The ionization cross-sections for the tyrosine molecule, which were measured in relative units, were normalized to the theoretical values, which allowed us to obtain their absolute values. The results of earlier HF calculations of the single-ionization cross-sections for the tyrosine and threonine molecules were presented in work [11], and, for some other amino acid molecules, in works [12, 13]. The ionization potentials of the examined molecules were evaluated theoretically on the basis of the binding energies of their highest occupied MOs (HOMOs).

Note that similar calculations of the energy parameters of molecules using the indicated theoretical methods that are based on the first principles were performed by us in works [14–16] while describing the characteristics of some organic and inorganic molecules and their positive fragment ions. In particular, the appearance energies for fragment ions at the dissociative ionization of the SF_6 molecule were obtained in works [14, 15], and for the CH_4, C_2H_6, and $S_n (n = 2 \div 8)$ molecules in work [16].

2. Experimental Technique to Study Single-Ionization of Molecules

Two kinds of ionization cross-sections are usually measured experimentally: these are total ionization cross-sections (when all positive fragment ions of various masses are registered) and single-ionization cross-sections (when only singly charged positive ions of a certain mass are registered). In the former case, if the energies are low and close to the threshold, the total experimental cross-section of ionization is determined exactly via the single-ionization cross-section of parent molecules. In the latter case, if the mass of a certain fragment ion is fixed, it is possible to directly measure the cross-section of the dissociative single-ionization process and determine the appearance energy of this fragment. If this is the mass of the ion of just the parent molecule, then the cross-section and the threshold of its single-ionization will be measured in the direct experiment.

The experimental setup used in our study was based on a modernized [17] and completely auto-

mated, on the basis of an IBM computer, magnetic mass spectrometer MI1201 (Fig. 1). The interval of working masses of the mass spectrometer was $m/z = 1 \div 600$ amu at the high sensitivity (10^{-16} A) and resolution (± 0.25 amu).

A beam of tyrosine molecules with a concentration of 10^{10} mol/cm^3 was generated by an effusive source at an operating temperature not higher than 150°C, which allowed the thermal destruction of the working substance to be avoided. A three-electrode electron gun [17] served as a source of the electron beam with a current of 30–50 μA. The useful signal was registered in a completely automatic mode, which was controlled making use of a personal computer, at a fixed electron energy. The researched substance (amino acid molecules) in the form of finely dispersed powder was placed in an effusion cell, which was heated up to the required temperature. The latter was stabilized making use of a digital thermometer with an accuracy of ±0.5°C. After the installation operating mode had been stabilized, the molecular and electron beams were brought into their optimal operating modes. The molecular beam was directed into an ionic source of a mass spectrometer (see Fig. 1), where it intersected with the electron beam.

The mixture of positively charged molecular fragments (M^+ in Fig. 2) that were formed in the ion source and pulled out of this source by the electric field entered a magnetic ion mass analyzer. At the analyzer output, the ions with a definite mass were registered with the help of an electrometer (see Fig. 1).

The system for collecting and processing experimental data made it possible to control the scanning of the mass analyzer and the energy of ionizing electrons by means of a personal computer (Fig. 1). Special measures were taken to stabilize the transmission of ions by the mass analyzer, which allowed us to reliably register the definite mass of the examined fragment (in our case, it was the mass of a tyrosine molecule, $m/z = 181$). The electron energy scale was calibrated according to the known ionization thresholds of the argon atom and the nitrogen molecule [10] with an accuracy not worse than ±0.2 eV.

If a certain mass is fixed, the energy dependence of the yield of this ion can be measured. The electron energy was varied in a step-like regime with an increment of 0.5 eV. The experimental value of the appearance threshold for the ions of a tyrosine molecule was

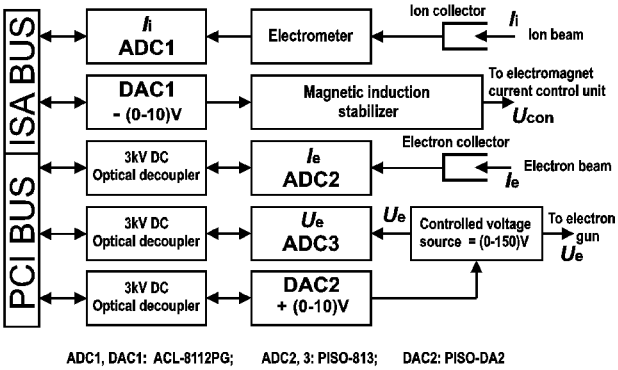

Fig. 1. Schematic diagram of the automated installation for measuring the mass spectra and energy dependences of the peak intensities of molecular fragments on the basis of modernized MI1201 magnetic mass spectrometer

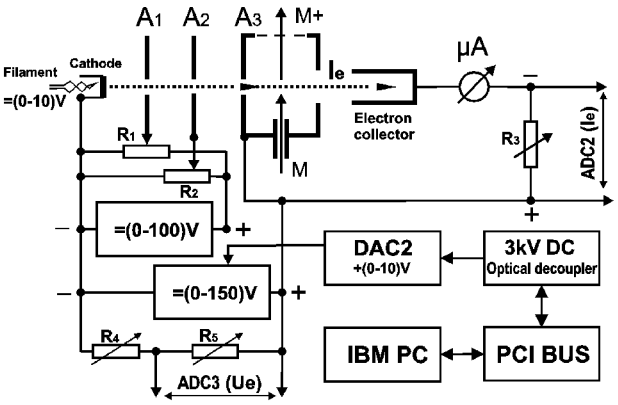

Fig. 2. Power supply scheme for the electron-optical system of a mass spectrometer and the registration of its parameters

determined using the fitting technique. The latter was based on the least-squares approximation and the application of the Marquardt–Levenberg algorithm [18].

In the direct experiment, we have measured the single-ionization cross-section of the parent tyrosine molecule. Owing to the low yield of singly ionized threonine molecules, the ionization cross-section of this molecule has not been measured. Furthermore, it cannot be ruled out that such ions are unstable. Figure 3 illustrates the energy dependence of the single-ionization cross-section of a tyrosine molecule in the electron energy interval from 0 to 70 eV. The cross-section measurement error did not exceed 40%. The molecular ionization threshold was 8.6 ± 0.1 eV. Calculations in work [10] gave a value of 7.94 eV, which is close to the indicated one.

3. Expressions for Calculating the Electron-Impact Single-Ionization Cross-Sections of Molecules

When evaluating the total (over the accounted MOs) single-ionization cross-sections of molecules, $\sigma(E) = \sum_k \sigma_k(E)$, the following models of pair collisions are applied: the dipole one (Binary–Encounter dipole one, BED), the semiclassical Bethe one (Binary–Encounter–Bethe one, BEB) [19–21], and the classical Gryzinski approximation (Gryz) [22] (see also work [23]).

In the BEB model, the expression for the cross-section of the molecular ionization (the removal of an electron) of the kth MO looks like (for the MO enumeration, see Table 1)

$$\sigma_k(t_k) = \frac{S_k}{t_k + u_k + 1}\left\{\frac{1}{2}Q_k\left(1 - \frac{1}{t_k^2}\right)\ln t_k + \right.$$

$$\left. + \left(2 - Q_k\right)\left[\left(1 - \frac{1}{t_k}\right) - \frac{\ln t_k}{t_k + 1}\right]\right\}. \quad (1)$$

Here, $t_k = E/B_k$, E is the kinetic energy of the incoming electron, B_k is the binding energy of the electron removed from the kth MO, $u_k = U_k/B_k$, and U_k is the average kinetic energy of electrons in the kth MO. The quantities S_k and Q_k are determined from the expressions

$$S_k = 4\pi a_0^2 N_k (R/B_k)^2, \quad Q_k = \frac{2B_k M_k^2}{N_k R}, \quad (2)$$

where

$$M_k^2 = \frac{R}{B_k}\int\limits_0^\infty \frac{1}{w_k + 1}\frac{df(w_k)}{dw_k}dw_k,$$

$w_k = W/B_k$, $W = E - |B_k|$ is the kinetic energy of the removed electron, $df(w_k)/dw_k$ is the differential oscillator strength for the molecule, N_k is the number of electrons per MO, $R = 13.6058$ eV is the Rydberg constant, and $a_0 = 5.2918 \times 10^{-11}$ m is the Bohr radius (the atomic unit of length). The value of Q_k is considered equal to unity [19].

The expression for the cross-section of electron removal from the kth MO in the Gryzinsky approximation has the form

$$\sigma_k(t_k) = \frac{\sigma_0}{B_k^2}\frac{1}{t_k}\left(\frac{t_k - 1}{t_k + 1}\right)^{3/2}\left\{1 + \frac{2}{3}\left(1 - \frac{1}{2t_k}\right)\times\right.$$

$$\left.\times \ln\left[2{,}7 + (t_k - 1)^{1/2}\right]\right\}, \quad (3)$$

where $\sigma_0 = 6.56 \times 10^{-18}$ eV^2 m^2. In this approximation, the cross-section is determined only by the binding energy B_k of the electron in the MO.

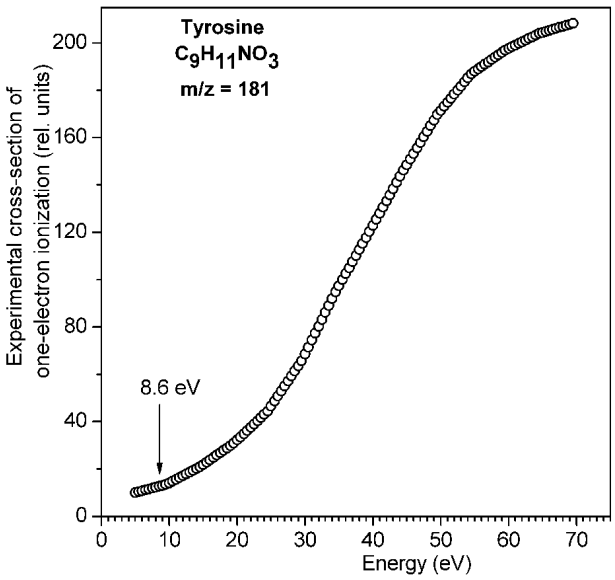

Fig. 3. Experimental energy dependence of single-ionization cross-sections of tyrosine molecule (in relative units). The arrow marks the ionization threshold

4. Theoretical and Experimental Results

4.1. Electron-impact single-ionization cross-sections of a tyrosine molecule

The cross-sections of the single-ionization process of the amino acid tyrosine molecule by the electron impact were calculated. The energy characteristics of 48 MOs of a tyrosine molecule (from the highest (outer) HOMO, $k = 48$, to the deepest one, $k = 1$) – namely, the binding energies B_k and the average electron kinetic energies U_k – were calculated in the framework of the HF method (HF/aug-cc-pVTZ) and the DFT methods with the help of the GAUSSIAN software package (version 09 Rev. E.01) [24] (see Table 1). On the basis of the binding energy B_{48}^{HOMO}, the ionization potentials of molecules were evaluated: $I(M) = -B_{48}^{\mathrm{HOMO}}$ (Koopmans' theorem). For the D-, L-, and Meta-forms of a tyrosine molecule, the calculated values are (in eV units):

Table 1. **Energy parameters B_k and U_k (in atomic units) of molecular orbitals (MOs) calculated for the D- and L-tyrosine molecules using the Hartree–Fock (HF) and density functional theory (DFT) methods**

No. of MO	D-tyrosine				L-tyrosine			
	HF		DFT		HF		DFT	
	$-B_k$	U_k	$-B_k$	U_k	$-B_k$	U_k	$-B_k$	U_k
14	1.4557	2.4943	1.1101	2.5464	1.4641	2.5028	1.1171	2.5551
15	1.3994	2.5368	1.0615	2.5862	1.4088	2.5299	1.0700	2.5774
16	1.3507	2.7902	1.0188	2.8590	1.3577	2.7990	1.0251	2.8647
17	1.1953	1.6832	0.8988	1.7517	1.2086	1.6152	0.9108	1.6797
18	1.1574	1.5079	0.8653	1.5572	1.1663	1.5526	0.8735	1.6013
19	1.0567	1.5518	0.7876	1.6104	1.0603	1.5845	0.7903	1.6444
20	1.0233	1.5423	0.7577	1.6009	1.0357	1.5581	0.7686	1.6161
21	0.9821	1.7124	0.7304	1.7928	0.9960	1.6656	0.7428	1.7369
22	0.9114	1.6270	0.6811	1.7139	0.9146	1.6809	0.6842	1.7821
23	0.8461	1.4141	0.6256	1.4592	0.8555	1.4239	0.6344	1.4834
24	0.8222	1.7521	0.6177	1.8369	0.8285	1.8130	0.6243	1.8583
25	0.7950	1.6407	0.5938	1.6589	0.8051	1.5641	0.6005	1.5863
26	0.7368	1.4991	0.5553	1.4862	0.7438	1.4944	0.5619	1.5098
27	0.7161	1.5082	0.5324	1.3951	0.7312	1.3877	0.5445	1.3177
28	0.6967	1.9891	0.5076	1.4172	0.6934	2.2374	0.5005	1.4091
29	0.6795	1.4481	0.4923	1.7616	0.6795	1.4470	0.4944	1.4882
30	0.6591	1.5118	0.4816	1.7073	0.6699	1.4704	0.4856	2.3175
31	0.6538	1.4787	0.4776	1.6890	0.6473	1.5766	0.4686	1.5802
32	0.6356	1.5148	0.4592	1.4666	0.6361	1.5398	0.4654	1.4532
33	0.6279	1.7377	0.4552	1.6743	0.6270	1.6698	0.4574	1.5636
34	0.6116	1.5460	0.4472	1.6324	0.6073	1.3468	0.4427	1.2883
35	0.5939	1.2152	0.4324	1.2458	0.6021	1.4528	0.4378	1.4971
36	0.5900	1.8579	0.4236	1.7552	0.5983	1.4786	0.4348	1.6565
37	0.5821	1.7131	0.4131	1.7936	0.5870	1.5999	0.4222	1.7227
38	0.5524	1.3669	0.3999	1.4949	0.5636	1.9032	0.3980	1.9052
39	0.5494	1.7197	0.3861	1.7350	0.5411	1.6278	0.3842	1.5613
40	0.5155	1.5654	0.3636	1.4558	0.5164	1.4266	0.3692	1.3689
41	0.4976	1.5680	0.3565	1.5080	0.5099	1.7120	0.3655	1.3794
42	0.4909	1.3335	0.3524	1.5377	0.5029	1.1516	0.3611	1.7825
43	0.4774	1.9446	0.3309	2.3022	0.4811	1.9503	0.3312	2.3432
44	0.4729	1.9763	0.3127	2.1986	0.4755	2.1386	0.3142	2.2729
45	0.4477	2.2317	0.2854	2.3725	0.4485	2.2576	0.2860	2.3822
46	0.3751	1.5922	0.2645	1.1526	0.4042	1.6510	0.2770	1.1631
47	0.3437	1.0381	0.2440	1.4361	0.3544	1.0586	0.2569	1.5492
48 HOMO	0.3235	1.2514	0.2329	1.6318	0.3329	1.2459	0.2508	1.5646

• the HF method: 8.8037 (D-Tyr), 9.0596 (L-Tyr), and 9.2127 (Meta-Tyr);

• the DFT method: 6.3383 (D-Tyr), 6.8238 (L-Tyr), and 6.8645 (Meta-Tyr).

One can see that the ionization potentials calculated using the HF method are close to an experimental value of 8.6 ± 0.1 eV. The calculations of thresholds based on the MO characteristics using the DFT

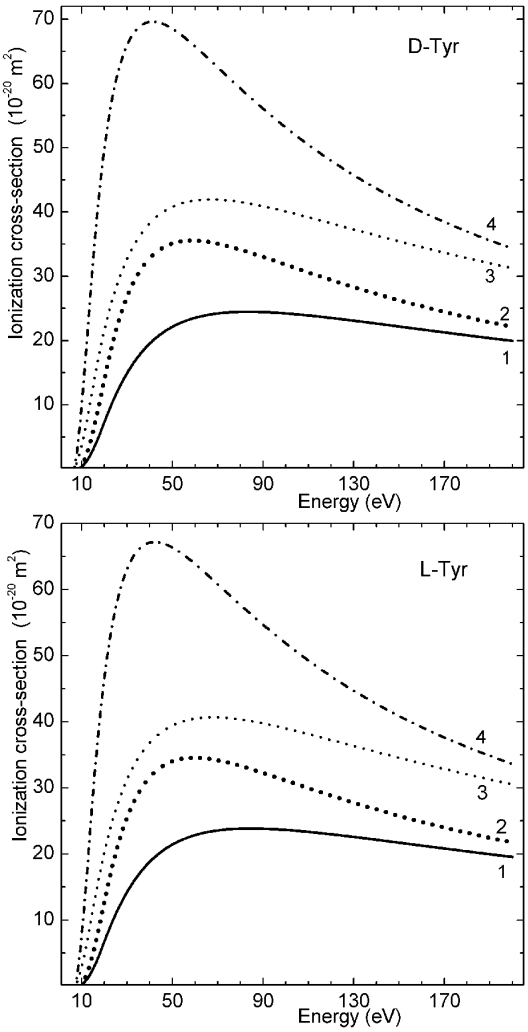

Fig. 4. Energy dependences $\sigma(E)$ of the total (over the accounted MOs) single-ionization cross-sections for the D- (upper panel) and L-forms (lower panel) of the tyrosine molecule calculated in various models: BEB-HF (*1*), Gryz-HF (*2*), BEB-DFT (*3*), and Gryz-DFT (*4*)

methods gave values lower by about 2 eV. In work [25], the value of B_{29}^{HOMO} calculated for glutamine and glutamic acid molecules using the HF method was by 4 eV higher than the same parameter calculated using the DFT method (see also work [12]). Recall that the calculation of the ionization potential in the adiabatic approximation – i.e., as the difference between the total energies of the molecule and its cation in their ground states – gives a more accurate value (see, for example, works [12, 25]). We can try, albeit inconsistently, to use these adiabatic ionization potentials when calculating the ionization cross-sections for the highest MO.

Table 1 contains the energy parameters for 35 MOs, from the above-mentioned 48 MOs, of the D- and L-forms of a tyrosine molecule, which were calculated using the HF and DFT methods, and whose binding energies are lower than 10 au (about 270 eV). One can see that the difference between the corresponding values calculated for the D- and L-forms of this molecule in the framework of the same approach is small. The difference between the corresponding values obtained using different approaches is larger. Therefore, the behavior of the ionization cross-sections calculated for those molecular forms in the same approach can be very similar, and the cross-section values close.

On the basis of the parameters obtained for those MOs and using the BEB [Eqs. (1) and (2)] and Gryz [Eq. (3)] approximations, we calculated the electron-impact single-ionization cross-sections $\sigma_k(E)$ for a tyrosine molecule from the kth MO and got the total cross-sections $\sigma(E)$ (from the B_{48}^{HOMO} thresholds to 200 eV). The obtained results are shown in Fig. 4. One can see that the ionization cross-sections calculated for both forms of a tyrosine molecule really have similar energy behavior and close values. The ionization cross-section of the molecule in the D-form is slightly larger than in the L-form. We also see that the cross-section calculated in the Gryz approximation grows faster with the energy than the cross-section in the BEB approximation. In each approximation, the cross-sections from the MOs calculated using the DFT methods grow faster than the cross-sections from the MOs calculated using the HF method. The maxima of those cross-sections are characterized by the following values (in 10^{-20} m^2 units), see also work [11]:

• the D-form: 24.48 at 83.5 eV (BEB-HF), 41.96 at 66.5 eV (BEB-DFT), 35.56 at 58.5 eV (Gryz-HF), and 69.62 at 41.5 eV (Gryz-DFT);

• the L-form: 23.85 at 84.5 eV (BEB-HF), 40.68 at 68.0 eV (BEB-DFT), 34.57 at 59.5 eV (Gryz-HF), and 67.19 at 42.5 eV (Gryz-DFT).

4.2. Absolute values of experimental electron-impact single-ionization cross-sections for a tyrosine molecule

In the case where the total ionization cross-sections are measured, the normalization of their relative val-

Table 2. **Absolute experimental values of the electron-impact single-ionization cross-section for the tyrosine molecule**

E, eV	Cross-section, 10^{-20} m^2	E, eV	Cross-section, 10^{-20} m^2	E, eV	Cross-section, 10^{-20} m^2
5.0	1.165	27.0	6.394	49.0	19.453
5.5	1.209	27.5	6.641	49.5	19.727
6.0	1.253	28.0	6.888	50.0	19.927
6.5	1.297	28.5	7.135	50.5	20.127
7.0	1.341	29.0	7.382	51.0	20.327
7.5	1.385	29.5	7.629	51.5	20.527
8.0	1.429	30.0	7.968	52.0	20.727
8.5	1.473	30.5	8.308	52.5	20.927
9.0	1.517	31.0	8.648	53.0	21.127
9.5	1.560	31.5	8.987	53.5	21.327
10.0	1.647	32.0	9.327	54.0	21.527
10.5	1.734	32.5	9.667	54.5	21.727
11.0	1.821	33.0	10.006	55.0	21.844
11.5	1.907	33.5	10.346	55.5	21.96
12.0	1.994	34.0	10.686	56.0	22.076
12.5	2.081	34.5	11.025	56.5	22.192
13.0	2.167	35.0	11.321	57.0	22.308
13.5	2.254	35.5	11.617	57.5	22.425
14.0	2.341	36.0	11.912	58.0	22.541
14.5	2.427	36.5	12.208	58.5	22.657
15.0	2.544	37.0	12.504	59.0	22.773
15.5	2.660	37.5	12.799	59.5	22.889
16.0	2.776	38.0	13.095	60.0	22.971
16.5	2.893	38.5	13.391	60.5	23.052
17.0	3.009	39.0	13.686	61.0	23.133
17.5	3.126	39.5	13.982	61.5	23.215
18.0	3.242	40.0	14.283	62.0	23.296
18.5	3.358	40.5	14.583	62.5	23.377
19.0	3.475	41.0	14.884	63.0	23.459
19.5	3.591	41.5	15.184	63.5	23.540
20.0	3.748	42.0	15.485	64.0	23.621
20.5	3.905	42.5	15.785	64.5	23.703
21.0	4.061	43.0	16.086	65.0	23.753
21.5	4.218	43.5	16.386	65.5	23.803
22.0	4.375	44.0	16.687	66.0	23.852
22.5	4.532	44.5	16.986	66.5	23.902
23.0	4.688	45.0	17.261	67.0	23.952
23.5	4.845	45.5	17.535	67.5	24.002
24.0	5.002	46.0	17.809	68.0	24.052
24.5	5.159	46.5	18.083	68.5	24.102
25.0	5.406	47.0	18.357	69.0	24.152
25.5	5.653	47.5	18.631	69.5	24.202
26.0	5.900	48.0	18.905	70.0	–
26.5	6.147	48.5	19.179	70.5	–

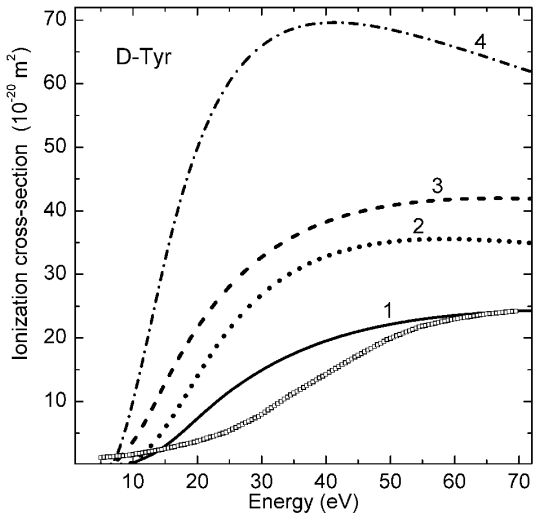

Fig. 5. Energy dependences $\sigma(E)$ of single-ionization cross-sections of the tyrosine molecule: experimental values normalized by the BEB-HF cross-section value calculated at the energy $E = 69.5$ eV (□); total (over the accounted MOs) single-ionization cross-sections of the D-tyrosine molecule calculated in various models: BEB-HF (*1*), Gryz-HF (*2*), BEB-DFT (*3*), and Gryz-DFT (*4*)

ues by the theoretical single-ionization cross-sections at energies close to the ionization thresholds makes it possible to obtain the absolute values of experimental data (see work [23]). Such a normalization of the relative values of the experimental ionization cross-sections obtained when registering the ion of the parent molecule by theoretical data can be carried out for any energy. The normalization also allows one to obtain the absolute values of the measured cross-sections. In the case of registration of ion fragments with a definite mass, the experimental cross-sections should be normalized by the theoretical values of dissociative single-ionization cross-sections.

In Fig. 5, we made the comparison between the energy dependence of the single-ionization cross-section of a tyrosine molecule measured up to 69.5 eV (see also Fig. 3) and the dependences $\sigma(E)$ for the total cross-section calculated for the D-form of this molecule in the framework of the indicated BEB and Gryz approximations (see also Fig. 4). One can see that, in terms of its energy behavior, it is the BEB-HF cross-section that is similar to the experimental one. Its threshold is also close to the experimental value. The absolute cross-section values corresponding to the relative experimental ones were calculated

Table 3. **Energy parameters B_k and U_k (in atomic units) of molecular orbitals (MOs) calculated for the D-, L-, D-Allo-, and Allo-threonine molecules calculated using the Hartree–Fock method**

No. of MO	D-threonine		L-threonine		D-Allo-threonine		Allo-threonine	
	$-B_k$	U_k	$-B_k$	U_k	$-B_k$	U_k	$-B_k$	U_k
9	1.4584	2.5003	1.4631	2.4985	1.4630	2.4927	1.4618	2.4965
10	1.3776	2.4768	1.3775	2.4496	1.3657	2.4880	1.3758	2.4753
11	1.3495	2.8003	1.3547	2.8038	1.3565	2.7961	1.3558	2.7979
12	1.1974	1.7363	1.2109	1.7766	1.1991	1.7491	1.2105	1.7263
13	1.0428	1.5717	1.0477	1.5570	1.0362	1.6093	1.0405	1.6145
14	0.9772	1.4989	0.9819	1.4909	0.9687	1.5239	0.9819	1.5155
15	0.8611	1.7454	0.8644	1.7286	0.8580	1.6413	0.8659	1.6515
16	0.8048	1.7155	0.8121	1.7074	0.8147	1.6666	0.8178	1.6720
17	0.7322	1.4169	0.7353	1.4190	0.7232	1.5899	0.7413	1.4231
18	0.7100	1.3636	0.7020	1.4763	0.7066	1.4026	0.6923	2.2464
19	0.6859	2.3058	0.6928	2.2048	0.6939	2.2218	0.6867	1.5644
20	0.6514	1.5373	0.6588	1.4220	0.6488	1.4524	0.6566	1.4324
21	0.6277	1.5500	0.6527	1.5186	0.6336	1.7517	0.6505	1.4945
22	0.6226	1.6418	0.6259	1.8300	0.6293	1.6224	0.6225	1.8824
23	0.6090	1.7188	0.6071	1.7047	0.5956	1.6932	0.6063	1.6981
24	0.5811	1.6615	0.5865	1.6200	0.5872	1.8917	0.5836	1.4920
25	0.5637	1.5762	0.5622	1.4962	0.5608	1.4432	0.5551	1.5212
26	0.5447	1.4814	0.5447	1.7119	0.5405	1.5569	0.5503	1.8767
27	0.5359	1.7161	0.5401	1.5540	0.5308	1.3092	0.5429	1.4518
28	0.5121	1.7486	0.5097	1.7071	0.4876	2.0494	0.5150	1.5917
29	0.4702	2.0811	0.4742	2.0580	0.4818	1.7271	0.4845	2.0328
30	0.4599	2.0961	0.4711	2.2094	0.4573	2.3272	0.4655	2.1884
31	0.4381	2.2524	0.4442	2.1863	0.4395	2.0987	0.4495	2.2241
32 HOMO	0.4022	1.6868	0.4123	1.7708	0.4084	1.7659	0.4037	1.8231

by normalizing the latter by the theoretical data calculated for the D-form of the molecule in the BEB-HF approximation at an energy of 69.5 eV, i.e., almost at the point of cross-section maximum. The absolute values for the measured single-ionization cross-sections of a tyrosine molecule are quoted in Table 2.

4.3. Electron-impact single-ionization cross-sections of a threonine molecule

We also carried out calculations for the electron-impact single-ionization cross-sections of a threonine amino acid molecule. The energy characteristics – the binding energies B_k and the average electron kinetic energies U_k – were calculated using the HF method [24] for 32 MOs of a threonine molecule (from the highest (outer) HOMO, $k = 32$, to the deepest one, $k = 1$) (see Table 3). On the basis of the binding energy B_{32}^{HOMO}, the ionization potentials of the molecule were evaluated: $I(M)$=$-B_{32}^{\mathrm{HOMO}}$ (Koopmans' theorem). For the D-, L-, D-Allo-, and Allo-forms of a threonine molecule, the obtained values are (in eV units): 10.9445 (D-Thr), 11.2193 (L-Thr), 11.1132 (D-Allo-Thr), and 10.9853 (Allo-Thr). One can see that the ionization potentials of the indicated forms of this molecule are close in magnitude and approximately equal to 11 eV.

Table 3 contains the energy parameters for 24 MOs – from the highest (outer) HOMO, $k = 32$, to the deep one, $k = 9$ – taken from 32 MOs of the D-, L-, D-Allo-, and Allo-forms of a threonine molecule

calculated using the HF method. Only the MOs with binding energies lower than 10 au (about 270 eV) were taken into account. One can see that the differences between the corresponding values for the indicated forms of this molecule are small. Therefore, the behavior of the ionization cross-sections of those molecular forms is expected to be very similar, and the cross-section values close.

Using the parameters of those MOs and the indicated BEB [Eqs. (1) and (2)] and Gryz [Eq. (3)] approximations, we calculated the electron-impact single-ionization cross-sections $\sigma_k(E)$ of a threonine molecule from the kth MO and obtained the total $\sigma(E)$ cross-sections (from the B_{32}^{HOMO} thresholds to 200 eV). The corresponding results are shown in Fig. 6. One can see that the ionization cross-sections calculated for both forms of a threonine molecule really have similar energy behaviors and close values. The ionization cross-section for the D-form of the molecule is somewhat larger than that for the L-form. One can also see that the cross-section calculated in the Gryz approximation grows faster than the cross-section calculated in the BEB approximation.

The maxima of those cross-sections are characterized by the following values (in 10^{-20} m^2 units):

• the D-form: 15.04 at 90.0 eV (BEB-HF) and 22.37 at 62.0 eV (Gryz-HF);

• the L-form: 14.80 at 91.0 eV (BEB-HF) and 21.97 at 62.5 eV (Gryz-HF).

They are somewhat shifted toward higher energies as compared to their counterparts for a tyrosine molecule. The values of the cross-sections for a threonine molecule at their maximum are about 1.5 times smaller than those for a tyrosine molecule (see above). This is a consequence of the energy structure of these molecules. In particular, for collision energies up to 200 eV, 35 MOs of the calculated 48 MOs contribute to the cross-section in the case of a tyrosine molecule, and only 24 of 32 MOs in the case of a threonine molecule.

4.4. HOMO contributions to electron-impact single-ionization cross-sections of tyrosine and threonine molecules

Consider the contributions from the HOMO to the total single-ionization cross-section of molecules. Its

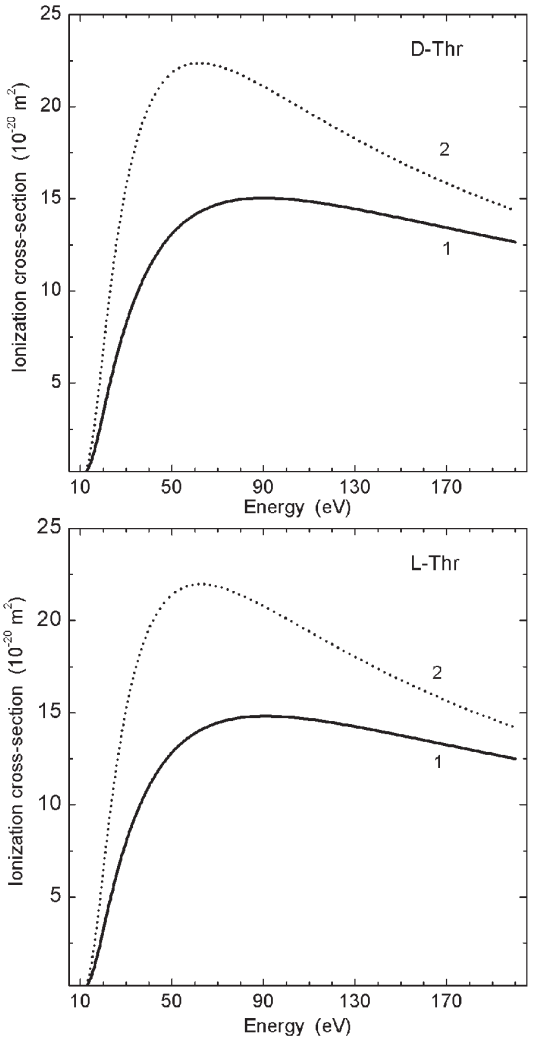

Fig. 6. Energy dependences $\sigma(E)$ of the total (over the accounted MOs) single-ionization cross-sections for the D- (upper panel) and L-forms (lower panel) of the threonine molecule calculated in the BEB-HF (*1*) and Gryz-HF (*2*) models

relative contribution equals

$$P(E) = \left[\frac{\sigma_{k_{\mathrm{HOMO}}}(E)}{\sum_{k=k_{\mathrm{HOMO}}}^{k=(k_{\mathrm{HOMO}}-n+1)} \sigma_k(E)}\right] 100\%.$$

Here, k is the MO number (see Tables 1 and 3), and n is the number of MOs taken into account for a given energy. The contribution from the HOMO is decisive at initial energies.

In Fig. 7, the energy dependence $P(E)$ of the relative contribution of the HOMO to the total cross-

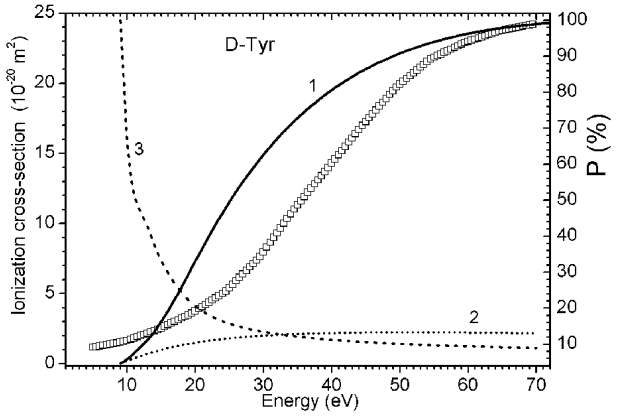

Fig. 7. Energy dependences of single-ionization cross-sections for the D-tyrosine molecule: experimental values normalized by the BEB-HF cross-section value calculated at the energy $E = 69.5$ eV (□); calculated BEB-HF characteristics: total single-ionization cross-section $\sigma(E)$ *(1)*, $\sigma_{k_{\rm HOMO}}(E)$ *(2)*, relative contribution $P(E)$ to the total single-ionization cross-section from the HOMO ($k_{\rm HOMO} = 48$)

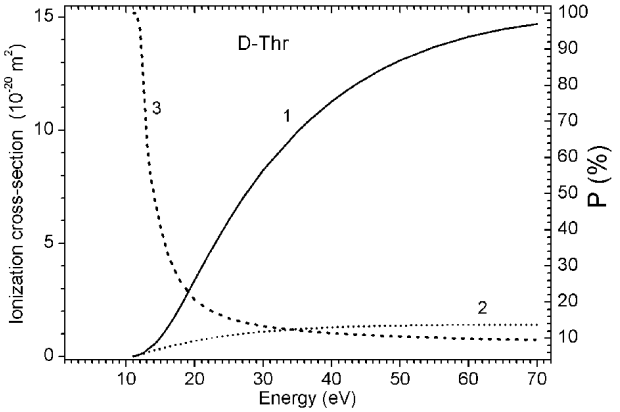

Fig. 8. Energy dependences of single-ionization cross-sections calculated for the D-threonine molecule in the BEB-HF model: total single-ionization cross-section $\sigma(E)$ *(1)*, $\sigma_{k_{\rm HOMO}}(E)$ *(2)*, and relative contribution $P(E)$ to the total single-ionization cross-section from the HOMO ($k_{\rm HOMO} = 32$)

section $\sigma(E)$ is compared with the absolute single-ionization cross-section values measured for a tyrosine molecule (see Fig. 5 and Table 2). The dependence $\sigma(E)$ calculated in the BEB-HF approximation for the total single-ionization cross-section of the molecule in the D-form and the dependence for the single-ionization cross-section $\sigma_{k_{\rm HOMO}}(E)$ are also exhibited. The magnitude of the contribution $P(E)$ and the number n of MOs in the total cross-section depend on the collision energy. The contribution decreases rapidly with the increasing collision energy. From Fig. 7, one can see that the HOMO contribution $P = 100\%$, i.e., the total cross-section is determined exclusively by the HOMO ($n = 1$), only at the ionization threshold, where $B_{48}^{\rm HOMO} = -8.817$ eV. Starting from 40 eV, the total cross-section is determined by all 35 MOs ($n = 35$). In general, the contribution of the HOMO is quite substantial: about 33% at 15 eV, about 13.5% at 30 eV, about 10% at 50 eV, and about 10% at 70 eV.

In Fig. 8, similarly to Fig. 7, the energy dependence $P(E)$ of the relative contribution of the HOMO to the total ionization cross-section $\sigma(E)$, but for a threonine molecule, is depicted. Also shown are the calculated dependence $\sigma(E)$ for the total BEB-HF cross-section of the single-ionization of this molecule in the D-form and the single-ionization cross-section dependence $\sigma_{k_{\rm HOMO}}(E)$. The values of the contribution $P(E)$ and the number n of MOs in the total cross-section depend on the collision energy. This contribution rapidly decreases with the increasing collision energy. From Fig. 8, one can see that $P = 100\%$ up to an energy of 11.5 eV, i.e., the total cross-section is determined only by the HOMO. Starting from 40 eV, the total cross-section is determined by all 24 MOs. In general, the HOMO contribution P is rather substantial: about 41% at 15 eV, about 13.5% at 30 eV, about 10.5% at 50 eV, and about 9.5% at 70 eV.

The behavior of the dependence $\sigma_{k_{\rm HOMO}}(E)$ for the orbital single-ionization cross-sections of both molecules in the D-form is similar. At the same time, the orbital ionization cross-section of a tyrosine molecule is regularly larger than that of a threonine molecule.

It is worth comparing the electron-impact ionization cross-sections for a number of biomolecules. In work [2], the following maximum values of the total effective ionization cross-sections were measured: $(28 \pm 6) \times 10^{-20}$ m^2 at 90 eV for an adenine molecule, and $(32 \pm 7) \times 10^{-20}$ m^2 at 88 eV for a guanine one. The theoretical values of the single-ionization cross-sections in the maxima at energies of 75–85 eV, which were calculated in work [5] in the BEB-HF approximation, are as follows (in 10^{-20} m^2 units): 21.84 (guanine), 20.46 (adenine), 17.61 (thymine), 16.58 (cytosine), and 14.57 (uracil). The single-ionization cross-sections at the maximum calculated in the

BEB-HF approximation are as follows (in 10^{-20} m^2 units): 28.82 at 67 eV (D-valine), 18.25 at 82.5 eV (D-glutamine), and 17.27 at 92 eV (D-glutamic acid) [12, 13, 23, 25], with the cross-section values obtained for the L-form of the molecules being almost the same. Thus, the total ionization cross-sections of the molecules exceed their single-ionization cross-sections. The calculated single-ionization cross-sections for the indicated biomolecules are close in magnitude. Perhaps, this is a quantitative property of the process of biomolecular ionization.

5. Conclusions

The energy dependence of the electron-impact single-ionization cross-section for a tyrosine amino acid molecule at energies up to 70 eV has been measured experimentally. The threshold for this process is determined to equal 8.6 ± 0.1 eV.

The electron-impact single-ionization cross-sections within the interval of collision energies from the ionization threshold to 200 eV are calculated for the L- and D-forms of tyrosine and threonine amino acid molecules in the framework of the Binary–Encounter–Bethe and Gryzinski approximations. The characteristics of molecular orbitals required for calculations are determined using the Hartree–Fock and density functional theory methods. The calculated ionization cross-sections for both forms of tyrosine and threonine molecules have similar energy behavior and close values. In general, the ionization cross-sections for a tyrosine molecule exceed the ionization cross-sections for a threonine molecule at all energies, being approximately 1.5 times larger at their maxima.

The ionization cross-sections measured for a D-tyrosine molecule are compared with the calculated ones. The comparison shows that the cross-section obtained in the Binary–Encounter–Bethe approximation with molecular orbitals calculated using the Hartree–Fock method better reproduces the experimental energy behavior of this parameter. It allowed us to normalize the relative values of the experimental single-ionization cross-sections for a tyrosine molecule by their calculated values and obtain the absolute values for the experimental ionization cross-section for this molecule. At an electron energy of 69.5 eV, which is close to the cross-section maximum, this quantity reaches a value of 24.202×10^{-20} m^2.

The main contribution to the calculated single-ionization cross-sections for tyrosine and threonine molecules at initial energies is made by the ionization cross-sections of the highest molecular orbital. This contribution decreases rather quickly with the collision energy growth. At an energy of 70 eV, which is close to the cross-section maxima, this contribution reaches almost 10%.

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ІОНІЗАЦІЯ МОЛЕКУЛ
АМІНОКИСЛОТ ТИРОЗИНУ
ТА ТРЕОНІНУ ЕЛЕКТРОННИМ УДАРОМ

Для молекули амінокислоти тирозину виміряно енергетичну залежність перерізу процесу однократної іонізації електронним ударом та визначено його поріг. Нормуванням відносного перерізу іонізації, одержаного в експерименті, на теоретичні величини визначено абсолютні значення перерізу. Потенціали іонізації молекул тирозину та треоніну оцінено теоретично за енергією зв'язку їхньої найвищої зайнятої орбіталі. Характеристики молекулярних орбіталей було розраховано за методами Хартрі–Фока та теорії функціонала густини. Перерізи однократної іонізації D- та L-форм вказаних молекул оцінено у моделі Binary-Encounter-Bethe та за формулою Гризінського.

Ключові слова: амінокислота, потенціал іонізації, молекулярна орбіталь, переріз іонізації.