Electron-driven processes in enantiomeric forms of glutamic acid initiated by low-energy resonance electron attachment

Stanislav A. Pshenichnyuk[1*], Nail L. Asfandiarov[1], Rustam G. Rakhmeyev[1], Alexei S. Komolov[2], and Oleg E. Tereshchenko[3,4]

[1] Institute of Molecule and Crystal Physics, Ufa Federal Research Centre, Russian Academy of Sciences, Prospeкt Oktyabrya 151, 450075, Ufa, Russia

[2] St. Petersburg State University, Universitetskaya nab. 7/9, 199034, St. Petersburg, Russia

[3] Rzhanov Institute of Semiconductor Physics, Siberian Branch, Russian Academy of Sciences, Lavrentyev Prospeкt 13, 630090, Novosibirsk, Russia

[4] Synchrotron Radiation Facility SKIF, Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Prospeкt Nikolsky 1, 630559, Koltsovo, Russia

Abstract

Low-energy (0-14 eV) resonance electron interaction and fragment species produced by dissociative electron attachment (DEA) for enantiomeric forms of glutamic acid (Glu) are studied under gas-phase conditions by means of DEA spectroscopy and density functional theory calculations. Oppositely to a series of the amino acids studied earlier employing DEA technique, the most abundant species are not associated with elimination of a hydrogen atom from the parent molecular negative ion. Besides this less intense closed-shell $[Glu - H]^-$ fragment, only two mass-selected negative ions, $[Glu - 19]^-$ and $[Glu - 76]^-$, are detected within the same electron energy region with the yield maximum observed at around 0.9 eV. This value matches well the energy of vertical electron attachment into the lowest normally empty π^* COOH molecular orbital of Glu located at 0.88 eV according to the present B3LYP/6-31G(d) calculations. Although the detection of asymmetric DEA properties *a priori* is not accessible under the present experimental conditions, a "chirality non-conservation" can be associated with some decay channels. Evidently, the measured spectra for the L- and D-forms are found to be identical, the results, nevertheless, being of interest for the forthcoming experiments utilizing spin-polarized electron beam as a chiral factor in the framework of conventional DEA technique.

Keywords: resonance electron scattering; shape resonances; dissociative electron attachment; amino acids; electron-triggered processes; molecular chirality

* Corresponding author. E-mail: sapsh@anrb.ru

I. Introduction

Single amino acid molecules represent the elementary building blocks of peptides and proteins which, in turn, can be considered as basic structures of all living organisms on Earth. Electronic properties of individual amino acid molecules are of importance to understand the elementary electron-driven reactions initiated by low-energy (0-14 eV) resonance electron scattering *via* a process known as dissociative electron attachment (DEA) [1-5]. In fact, DEA is associated with indirect DNA damage caused by the formation of temporary negative ion (TNI) states of various DNA components (base, phosphate, deoxyribose) with the secondary electrons [6-8]. These low-energy (<20 eV) electrons originate in living tissues as a result of exposure to high-energy (millions electronvolts) radiation [9], and are responsible for generation of DNA single- and double-strand breaks as well as for loss of supercoiled DNA [10]. It is to be noted that despite many others, as a rule extremely complex, biological processes, the underlying reactions of the low-energy secondary electrons in biological tissues have been understood on the molecular level owing to detailed DEA studies of biorelevant molecular structures [11-13].

The analogous mechanism can reasonably be linked with radiative damages in another class of important biomolecules – peptides and proteins [14], where the processes of formation and decay of TNI states of individual amino acid molecules are expected to play a vital role [15-17]. Therefore, studies of electron-triggered reactions, particularly DEA, for amino acids are necessary to understand the whole picture of the radiative effects produced by high-energy particles in the cells of living organisms. Due to high reactivity of the secondary slow electrons, their interaction with amino acids in living tissues through the resonance processes can also dramatically influence the most crucial metabolic pathways within the organism. In fact, these pathways involve amino acids as principal metabolic products [18,19] and their disruption, in turn, can be linked with many pathological conditions [20]. Additionally, the results of DEA studies for amino acids can be of importance in many applied fields linked with (i) radiative protection on the facilities with increased risk like nuclear power stations and spacecraft under manned long-term missions [21,22], (ii) radiative exposure under conditions of radiosensitization and radiation therapy [23,24].

Nuclear proteins like histones being in close contact with DNA are involved in the DNA packaging and replication providing also the protection from tangling and other damages. Therefore, there exists an obvious interplay between DNA, microsomal proteins and possible active radical species produced by the secondary low-energy electrons. In fact, the protective role of amino acids has been recently demonstrated under electron attachment to DNA when the amino acid molecule (i) acts as a physical shield preventing interaction of the nucleobase with incoming electron and (ii) stabilizes the nucleobase TNI state thus suppressing rupture of the

sugar-phosphate bond [25]. The protective activity has been also ascribed to ability of the amino acids to thermalize electrons [17]. Much lower DNA damages have been reported using a fluorescence method in case of formation of the complex of oligonucleotides with a single-strand-binding protein [26], whereas protection of the DNA tetramer by glycine and arginine against DEA damage have been found to be concentration dependent [27]. In this context substituted amino acids and simple peptides can serve as model systems to understand the mechanisms of resonance electron interaction with proteins *via* the simplest processes linked with the cleavage of peptide bonds and disulfide bridges [28], the latter being found much more sensitive to slow electron attack [14]. Accordingly, DEA-studies have been reported for N-acetyl derivatives of tryptophan and glycine [29,30] as well as for N-methyl derivatives of glycine and alanine [31] to demonstrate the effective TNI decays at sub-excitation energies. A variety of the DEA-associated bond cleavage reactions has been also demonstrated for di- and tripeptides assembled from various combinations of the simplest amino acids, glycine and alanine [32-38].

Turning back to individual molecules, vertical electron attachment energies to form low-lying TNI states in a series of amino acids (glycine, alanine, phenylalanine, tryptophan, proline) have been measured [39] using electron transmission spectroscopy (ETS) [40-42] with a general observation of electron attachment into the normally empty π^* molecular orbital (MO) of COOH group. This MO can be solely detected in ETS for glycine and alanine at vertical attachment energies (VAEs) 1.93 and 1.80 eV, respectively, close to that (1.73 eV) detected in the reference formic acid, HCOOH [39]. Peak maxima detected in the total DEA cross-section (1.25 and 1.27 eV for glycine and alanine, respectively) are considerably (0.68 and 0.53 eV, respectively) shifted from the positions of corresponding experimental VAEs, i.e., peak maxima detected in the total electron scattering cross-section. On this basis the dominant DEA channel at low electron energies has been attributed [43] to electron attachment into the normally empty σ^* MO associated with the OH bond, the conclusion being supported later using resonant R-matrix theory calculations [44]. The most abundant DEA signal in the low-energy range (1.2-1.3 eV) is associated with formation of the closed-shell fragment negative ions $[M - H]^-$, i.e., the parent molecular negative ion minis a hydrogen atom (M = target molecule), as demonstrated by many DEA-studies for glycine [45-49], alanine [45,46,51,51], valine [46,52-54], and leucine [55,56]. Absolute DEA cross-section has been reported for glycine and alanine to be an order of 10^{-16} cm^2 in mass-selected studies [45,48,50] and 10^{-19} cm^2 in the total negative ion yield measurements [43].

Glutamic acid (Glu, structure is reported in Fig.1), an aliphatic non-essential dibasic amino acid and a key metabolic compound, is not only included in protein synthesis of almost all living organisms on Earth, but also serves as the most abundant neurotransmitter and possesses a

variety of pharmacological activities [57-59]. Like many others amino acids, Glu is optically active compound: the molecule has one asymmetric carbon atom at position 2 (see Fig.1) that gives rise to two enantiomeric forms, the L-form being widely occurring in Nature. Evidently, chiral properties of Glu enantiomers are essential to understand the biochemical processes they involved in. Glu molecule is sufficiently different from the amino acids studied earlier by DEA technique due to presence of two COOH groups which, in turn, is associated with the most abundant DEA processes [45-56]. To the best of our knowledge, the investigations of electron interaction with Glu, likely, in its racemic mixture, are only limited to electron impact studies employing mass spectrometry to detect the positive ions [60,61]. Dissociative ionization of structurally close glutamine has been also studied under gas-phase conditions [61]. It should be noted that glutamine has been recently recognized as a key player in human metabolism also serving as a marker of many dangerous diseases by means of hyperpolarized magnetic resonance method [62].

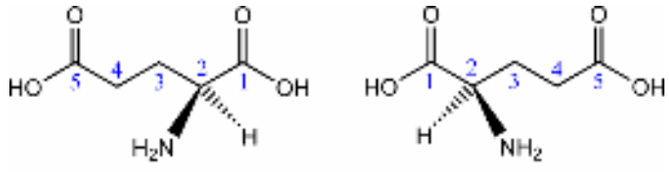


Fig.1. Molecular structures and atom labeling for enantiomeric forms of glutamic acid.

The present study reports DEA properties for enantiomeric forms of Glu that also concerns another important aspect which, however, *a priori* is not expected to be disclosed under the present experimental conditions. This is linked with detection of the differences between resonance electron scattering of the mirror conformers of chiral target molecules. Obviously, the only chiral factor that can make DEA spectroscopy sensitive to distinguish between optically active isomers is the asymmetric incident electron beam, which originates from the spin-polarized electron source [63]. Detection of asymmetry in the electron current transmitted through the camphor vapor has been found to produce somewhat contradicting results [64-66]. Halogenated camphor molecules have been used as chiral target irradiated by the polarized electron beam originated from GaAs-photocathode in the attempts to examine the Vester-Ulbricht hypothesis [67-69]. A small asymmetry of an order 10^{-4} in the total DEA cross-section has been reported to be most pronounces in case of the iodine derivative [68]. Since amino acids are suspected to play a vital role in the prebiotic synthesis [70,71], DEA studies of their enantiomers should be more attractive in the context of Vester-Ulbricht hypothesis that additionally motivates the present work. Indeed, selective decomposition of D-enantiomers should indicate that the L-form can be involved in asymmetrical synthesis of chirally clean

biological molecular assemblies, the conclusion being of importance to disclose one of the most intriguing puzzles of Universe – chiral asymmetry of life [72-74].

The present paper is aimed to show that DEA spectroscopy in its conventional scheme, i.e., without spin-polarized electron beam, is not able to distinguish between optically active isomers. Indeed, the present results testify for the similarity of (rather simple as shown below) DEA spectra for Glu enantiomers. Due to a variety of the dissociative channels of L- and D-tryptophan detected using the same experimental apparatus [75], the similarity of DEA spectra has been only tentatively concluded. Peak position for the $[M - H]^-$ formation by DEA to L- and D-alanine has been reported as 1.27 eV (at electron energy resolution 0.12 eV) [50] and 1.20 ± 0.030 eV [45], respectively, using different experimental apparatus, but can be considered equal within the error bars.

II. Experimental and Computational Procedures

A. DEA studies *in vacuo*

A general overview of DEA spectroscopy may be found elsewhere [1-5] including a schematic representation and description of specific conditions [76,77]. Briefly, a magnetically collimated electron beam of defined energy was passed through a collision cell containing a vapor of the substance under investigation, under single-collision conditions. A current of magnetically mass-selected negative ions was recorded as a function of the incident electron energy in the 0-14 eV energy range. The electron energy scale was calibrated with the SF_6^- signal at zero energy, generated by attachment of thermal electrons to SF_6. The full width at half maximum of the electron energy distribution was 0.4 eV, and the accuracy of the measured peak positions was estimated to be ±0.1 eV.

B. Thermal evaporation of Glu

The substances under investigation (L- and D-Glu enantiomers, Sigma-Aldrich #G1251 and G1001, respectively) were evaporated at 125 °C, that is, just below the reported melting points (around 200 ^{0}C stated by the manufacture). The walls of the collision cell were kept at 135 ^{0}C to prevent condensation. Since organic acids, in particular, amino acids may undergo thermal decomposition under their evaporation into vacuum, preparation of the molecular beam containing the intact target molecules must be carefully controlled. Melting properties of twenty amino acids have been recently measured using fast scanning calorimetry that allows to escape their decomposition upon slow heating. The reported values for the simplest amino acids are much higher that 200 ^{0}C, namely, 296 ^{0}C (glycine), 335 ^{0}C (alanine), 256 ^{0}C (valine), and 293 ^{0}C

(Glu) [78]. However, the amino acids tend to decompose before they melt, that may appear much below 200 ^{0}C under their evaporation into vacuum.

In particular, thermally stimulated degradation of COOH group may lead to elimination of CO_2 molecules from the amino acids [79]. Accordingly, the characteristic spectral feature at 3.57 eV can serve as marker of this undesirable process under conditions of ETS experiments as demonstrated in case of thermal destruction of cysteine at 136 ^{0}C [39] (melting point 331 ^{0}C [78]). Under DEA experiments, the m/z = 16 signal can clearly indicate the presence of CO_2 decomposition product since the current of O^- formed by DEA to CO_2 possesses the characteristic shape: two pronounced peaks located at 4.4 and 8.2 eV [80]. But neither in DEA study of cysteine (evaporation at 117 ^{0}C) [81] nor under the present experimental conditions with Glu evaporation up to 160 ^{0}C, the signature of O^- signal due to the CO_2 degradation product has not been detected.

Another decomposition pathway of the amino acids may be associated with thermally induced H_2O elimination as reported in DEA study of glycine by detection of the characteristic sharp H_2O electronic bands at the energy losses in the range 10–12 eV [45] under the evaporation temperatures above 170 ^{0}C. Thermal decomposition of Glu *via* H_2O elimination producing pyroglutamic acid (molecular weight 129 a.u.) has been detected in the positive ion mass spectrum under evaporation at 137 ^{0}C [60,61]. This finding is in agreement with the present observation of rapid rising of the m/z = 128 signal (non-proportional to the others) which can be associated with formation of $[M - H]^-$ by DEA to pyroglutamic acid that indicates the onset of Glu thermal destruction at evaporation temperatures above 140 ^{0}C. This process accompanied by melting and caramelization of the sample powder in the direct inlet probe of our experimental apparatus was not detected at above-stated evaporation temperature 125 ^{0}C. Therefore, it can be assumed that thermal decomposition of Glu enantiomers is negligible under the present experimental conditions. It is also to be noted that Glu DEA signals were very weak. therefore, the evaporation temperature was set to a maximal possible value to escape the decomposition but to detect the signals.

C. *In silico* methods

Density functional theory calculations were performed with the Gaussian 09 set of programs [82]. Evaluation of the virtual orbital energies (VOEs) of the neutral molecule was performed using the B3LYP hybrid functional with the minimal 6-31G(d) basis set, which does not contain diffuse functions. The adiabatic electron affinity was obtained as the energy difference between the neutral and the lowest anion state, each in its optimized geometry, using the standard 6-31+G(d) basis set. Regardless of particular difficulties encountered for the

description of anionic states [83], it has been demonstrated [42,84,85] that good linear correlations can be obtained between VAEs measured in ETS and the corresponding VOEs of the neutral molecules calculated with basis sets which do not include diffuse functions. The scaling parameters are different for σ* and π* MOs and a more accurate correlation would result if "training" compounds were employed that were structurally closer to the subject molecule. The σ* scaled VOEs evaluated with this procedure are generally less reliable than the π* scaled VOEs, due to the smaller number of experimental data available for the calibration. In the present study, the linear equation VAE = 0.8065×VOE + 0.9194, derived for the π* MOs of alternating phenyl and ethynyl groups [86] was employed to predict VAEs on base of the B3LYP/6-31G(d) π* VOEs. Certainly, the present calculations do not account for very small differences between the enantiomeric forms, thus, the results reported below are not distinguished for both Glu enantiomers.

III. Results and Discussion

A. Fragment species produced by DEA to gas-phase Glu

Oppositely to a series of the amino acids studied earlier [45-56], all the negative ion signals formed by DEA to Glu are observed in one electron energy region around 0.9 eV, and the $[Glu - H]^-$ (m/z = 146) is less intense decay as presented in Fig.2 for both L- and D-Glu forms. The results for two enantiomers are found to be identical. According to the present B3LYP/6-31+G(d) calculations of thermodynamic energy thresholds (reported in Table 1), H-atom elimination from the OH group attached to C-atom in position 5 (see Fig.1) provides the most energy benefit and is additionally consistent with localization properties of both the lowest π* LUMO and the lowest σ* OH LUMO+3 molecular orbitals associated with the $[Glu - H]^-$ peak (see Section III.B). However, the threshold for H-atom elimination from the other COOH group (attached to C-atom at position 1) does not contradict (on energetic grounds) with observation of the $[Glu - H]^-$ signal at 0.9 eV. Therefore, both processes leading to generation of the $[Glu - H]^-$ fragment by DEA to Glu can be experimentally accessible, the calculated values of Gibbs free energies reported in the last column of Table 1 being in agreement with this conclusion. When H-atom is initially abstracted from the amino group, the nearest COOH group (position 1) donates its H-atom to the NH site that leads to the same $[Glu - H]^-$ final structure (thus not presented in Table 1) and, in turn, to the same threshold (0.65 eV) according to the present calculations.

The most intense DEA signal is ascribed to formation of the $[Glu - 19]^-$ (m/z = 128) fragment that can be associated with elimination of either OH group and two H-atoms or NH_2

group and three H-atoms from the parent molecular negative ion. On energetic grounds, the former process can appear provided that the incoming electron brings more than 4 eV even in case of formation of the most stable neutral counterpart (H_2O molecule plus H-atom as compared with H_2 molecule plus $^{\bullet}OH$ radical) as shown in Table 1, therefore, cannot be accounted for the signal observed at 0.9 eV. However, cyclization accompanied by the H-atom migration in the $[Glu - OH - 2H]^-$ fragment to generate the dehydrogenated pyroglutamic acid negative ion lowers the threshold to 1 eV (ZPE-corrected value in Table 1) that, however, is less likely by the kinetic reasons. The most energy benefit is expected when the $[Glu - 19]^-$ fragment is formed by elimination of the NH_2 and three H-atoms, so that ammonia plus diatomic hydrogen molecules are generated as a neutral counterpart that considerably stabilizes the final products.

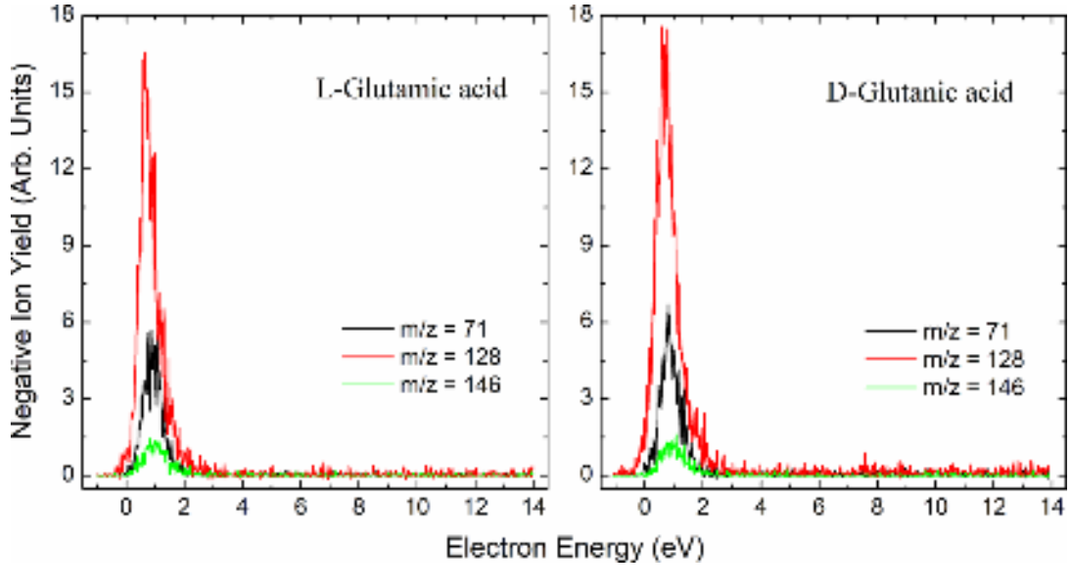


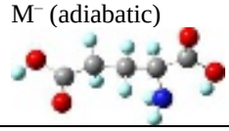
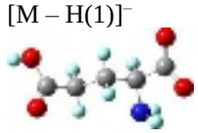
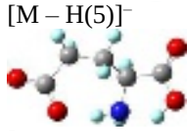
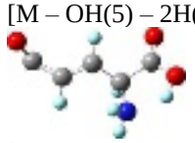
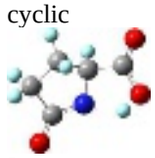
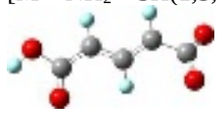
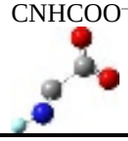
Fig.2. Mass-selected signals of the negative ions generated by DEA to Glu enantiomers.

Provided that the latter fragmentation pathway is accounted for generation of the $[Glu - 19]^-$ fragment, this process can serve as a model of the N-C_α bond cleavage in proteins as highlighted elsewhere [46]. In this context it should be noted that this decay in Glu is observed, and is possible on energetic grounds, at much lower incident electron energy (0.9 eV) as compared with all other amino acids. Indeed, the lowest maximum of the $[M - 19]^-$ signal peaks at around 5.5-6 eV in glycine, alanine, valine and leucine [46-48,50,53]. On basis of accurate mass measurements this signal has been assigned to sequential elimination of H-atom and H_2O molecule from the parent molecular negative ion, the reaction thus being accompanied by the complex rearrangements energetically permitted in the 5.5-6-eV energy range. On basis of the present calculations (see Table 1) alternative decay scheme for the formation of $[Glu - 19]^-$ at 0.9 eV should be suggested. Namely, the most energetically and kinetically efficient process is associated with elimination of ammonia and diatomic hydrogen that can occur without complex rearrangements of the molecular frame as schematically shown in Fig.3. It is to be noted that

approaching of the H-atom and amino group (to form NH_3) as well as two H-atoms (to form H_2) to each other can be stimulated by the excitation of Glu normal modes #9 and #18 as schematically shown in Fig.3.

Fig.3. Likely pathway for the elimination of NH_3 and H_2 from the parent molecular negative ion; schematic representation of corresponding B3LYP/6-31+G(d) normal vibrations and their frequencies.

Table 1. B3LYP/6-31+G(d) total energies relative to the ground state neutral molecules. The values in parentheses are ZPE (zero-point vibrational energies)-corrected. Gibbs free reaction energies are reported at 408K. All values are in eV.

M/z	Fragment structures [a)]		Chirality conservation	Relative energy	Free reaction energy
	Anion	Neutral			
147	M^- (adiabatic) 			0.32 (0.20)	
146	$[M - H(1)]^-$ 	$H^\bullet$	Yes	1.02 (0.65)	0.24
146	$[M - H(5)]^-$ 	$H^\bullet$	Yes	0.65 (0.30)	-0.03
128	$[M - OH(5) - 2H(3,4)]^-$ 	$H_2O + H^\bullet$	Yes	4.75 (4.10)	3.09
		$H_2 + {}^\bullet OH$	Yes	5.12 (4.40)	3.39
128	$[M - OH(5) - 2H(3,4)]^-$ cyclic 	$H_2O + H^\bullet$	Yes	1.54 (1.00)	0.13
128	$[M - NH_2 - 3H(1,3,4)]^-$ 	$NH_3 + H_2$	No	0.27 (-0.36)	-1.42
71	$C(H)NCOO^-$ 	$CH_3CH_2COOH + H_2$	No	0.61 (-0.03)	-1.27
71	$CNHCOO^-$ 	$CH_3CH_2COOH + H_2$	No	1.10 (0.49)	-0.70

Note: [a)] Chiral structures are reported for L-Glutamic acid.

Observation of the m/z = 71 fragment negative ion can be reasonably associated with elimination of two closed-shell neutral molecules, propionic acid and diatomic hydrogen, from the parent molecular negative ion, the threshold for the formation of the $C(H)NCOO^-$ structure being even negative as reported in Table 1. It should be mentioned that the cleavage of any bond associated with the asymmetrical carbon atom (position 2) leads to loss of the chirality in the DEA-products (as indicated in the last three rows of Table 1). This can be likely associated with "chirality non-conservation" or "mirror symmetry breaking" by DEA that, in turn, is linked with helicity conservation [87-89], but no corresponding "selection rule" can be concluded from the present experimental data.

B. Predicted VAEs and assignment of the TNI states

The presence of two COOH groups in dibasic Glu molecule is associated with two low-lying normally empty π* MOs which localization properties are schematically reported in Fig.4 along with predicted VAEs to form the TNI states *via* shape resonance mechanism [1-5]. And again, oppositely to almost all amino acids studied earlier [45-56], the maximum of the DEA cross-section for formation of the $[Glu - H]^-$ (0.9 eV) matches well the predicted position of the lowest π_1* VAE (0.88 eV), i.e., is not shifted to the lower energies by 0.4-0.7 eV as discussed earlier [43]. This likely indicates that the initial electron attachment into the π_1* MO is followed by distortions that couple π_1* to an antibonding σ* MO associated with the OH bond (also schematically represented in Fig.4) that, in turn, allows the H-atom elimination. This mechanism is analogous to that suggested earlier in case of DEA to DNA bases (thymine, cytosine, adenine), where production of $[M - H]^-$ has been observed within experimental error at the energies of the π* VAEs as discussed elsewhere [44]. Localization properties of the lowest π* COOH LUMO and σ* OH LUMO+3 (see Fig.4) on the same carboxylic group are in line with this coupling mechanism. Because of the absence of experimental ETS results for σ* resonances to form a scaling equation, predicted VAEs for σ* MOs are less reliable than that for π* states [43,90]. Nevertheless, using the same π* scaling, position of the σ* OH resonance in Glu is predicted to lie at 2.44 eV, or at 3.14 eV with a scaling obtained for the σ* (C-Cl) MOs of 13 chloroalkanes [91]. These values are in agreement with the rough estimate reported for a model compound HCOOH as 2.59 and 2.90 eV [43], respectively. Unfortunately, low electron energy resolution of the present experiment as well as very low intensities of the DEA signals are not sufficient to distinguish neither a vertical onset nor vibrational fine structures in the $[Glu - H]^-$ signal to support this assignment.

Finally, not only the dominant $[M - H]^-$ decay, but also some weak characteristic DEA signals have been observed for the amino acids [45-56] at relatively low incident electron energies, around the position of the π* COOH resonance. Indeed, the fragment negative ions $[M - 17]^-$ and $[M - 16]^-$ have been detected in the range 1.5-1.9 eV, i.e., on the right wing of the most intense $[M - H]^-$ signal in glycine, alanine, valine and leucine [46,47,50,52,53,55]. It can provide some additional confidence that the most intense m/z = 128 fragment observed in low energy resonance (0.9 eV) originates from DEA to Glu, but not linked with thermal decomposition of the target molecules.

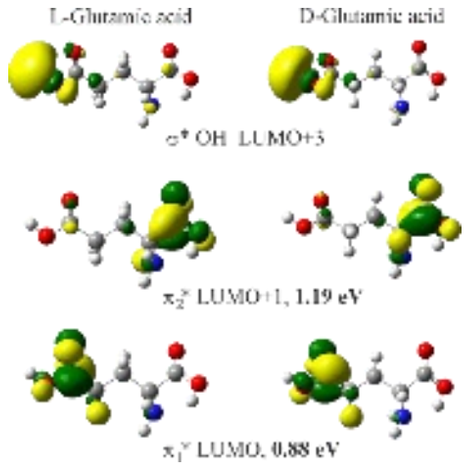


Fig.4. Schematic representation and predicted energies of electron attachment into the lowest two π* COOH and σ* OH normally empty MOs from B3LYP/6-31G(d) calculations of Glu enantiomers.

IV. Conclusions

Low-energy (0-14 eV) electron interaction with enantiomeric forms of glutamic acid is studied by mean of DEA spectroscopy under gas-phase conditions. Density functional theory calculations are employed to assign the experimental findings. The main conclusions are as follows:

1. DEA to Glu produces only three decay channels observed in a single resonance peak at around 0.9 eV, which are $[Glu - 76]^-$ (m/z = 71), $[Glu - 19]^-$ (m/z = 128) and [Glu – H]– (m/z = 146), the latter being less intense under the present experimental conditions.

2. The most intense DEA signal is associated with formation of the $[Glu - 19]^-$ fragment species that can be ascribed by the elimination of NH_2 group and three H-atoms from the parent molecular negative ion to form ammonia plus diatomic hydrogen as a neutral counterpart. However, despite its lower probability by kinetic grounds, the alternative pathway, namely, elimination of H_2O and H-atom accompanied by complex atom rearrangement to form the m/z = 128 cyclic structure, cannot be completely ruled out.

3. DEA cross-section for $[Glu - H]^-$ formation peaks at 0.9 eV, therefore, matches well position of the lowest π^* COOH resonance predicted to lie at 0.88 eV that can testify for direct electron attachment into the π^* LUMO state followed by its coupling to an antibonding σ^* OH resonance.

4. As *a priory* suggested, DEA spectra obtained for the Glu enantiomeric forms are found to be identical, that is evident but important conclusion in the context of the DEA experiments with spin-polarized electron beam.

5. Provided that any bond associated with asymmetrical carbon atom is cleaved, chirality initially presented in the target molecule disappears in the products that can be considered as DEA-stimulated "chirality non-conservation".

Finally, spin-polarized electron beam must be employed in conventional DEA experiment as a chiral factor to distinguish between DEA properties of optically active isomers and to study chiral-induced spin selectivity effects. The forthcoming experiments are under consideration to utilize both the recently suggested multi-alkali photocathode [92] as a source of low-energy spin-polarized electrons and the semiconductor heterostructure-based spin-detector [93-95] to estimate the electron beam polarization.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article and from the corresponding author upon reasonable request.

REFERENCES

[1] Schulz, G. J. (1973). Resonances in electron impact on diatomic molecules. Reviews of Modern Physics, 45(3), 423.

[2] Khvostenko, V. I., & Tolstikov, G. A. (1976). Application of the mass spectrometry of negative ions to organic chemistry. Russian Chemical Reviews, 45(2), 127-141.

[3] Christophorou L G Electron-molecule interactions and their applications (Orlando: Academic Press, 1984).

[4] Allan, M. (1989). Study of triplet states and short-lived negative ions by means of electron impact spectroscopy. Journal of Electron Spectroscopy and Related Phenomena, 48(2), 219-351.

[5] Illenberger E, Momigny J Gaseous molecular ions. An introduction to elementary processes induced by ionization (Steinkopff Verlag Darmstadt: Springer-Verlag, 1992)

[6] Boudaıffa, B., Cloutier, P., Hunting, D., Huels, M. A., & Sanche, L. (2000). Resonant formation of DNA strand breaks by low-energy (3 to 20 eV) electrons. Science, 287(5458), 1658-1660.

[7] Baccarelli, I., Bald, I., Gianturco, F. A., Illenberger, E., & Kopyra, J. (2011). Electron-induced damage of DNA and its components: Experiments and theoretical models. Physics Reports, 508(1-2), 1-44.

[8] Alizadeh, E., Orlando, T. M., & Sanche, L. (2015). Biomolecular damage induced by ionizing radiation: the direct and indirect effects of low-energy electrons on DNA. Annual review of physical chemistry, 66(1), 379-398.

[9] Solov'yov, A. V., Verkhovtsev, A. V., Mason, N. J., Amos, R. A., Bald, I., Baldacchino, G., ... & Solov'yov, I. A. (2024). Condensed matter systems exposed to radiation: Multiscale theory, simulations, and experiment. Chemical Reviews, 124(13), 8014-8129.

[10] Alizadeh, E., Orlando, T. M., & Sanche, L. (2015). Biomolecular damage induced by ionizing radiation: the direct and indirect effects of low-energy electrons on DNA. Annual Review of physical Chemistry, 66(1), 379-398.

[11] Sanche, L. (2002). Nanoscopic aspects of radiobiological damage: Fragmentation induced by secondary low-energy electrons. Mass Spectrometry Reviews, 21(5), 349-369.

[12] Narayanan SJ, J., Tripathi, D., Verma, P., Adhikary, A., & Dutta, A. K. (2023). Secondary electron attachment-induced radiation damage to genetic materials. ACS Omega, 8(12), 10669-10689.

[13] Pshenichnyuk, S. A., Asfandiarov, N. L., Markova, A. V., Komolov, A. S., Timoshnikov, V. A., & Polyakov, N. E. (2023). Elementary processes triggered in curcumin molecule by gas-phase resonance electron attachment and by photoexcitation in solution. The Journal of Chemical Physics, 159(21) 214305.

[14] Sanche, L. (2005). Low energy electron-driven damage in biomolecules. The European Physical Journal D-Atomic, Molecular, Optical and Plasma Physics, 35, 367-390.

[15] Aldrich, J. E., Lam, K. Y., Shragge, P. C., & Hunt, J. W. (1975). Fast electron reactions in concentrated solutions of amino acids and nucleotides. Radiation Research, 63(1), 42-52.

[16] Tal, Y., & Faraggi, M. (1975). The reaction of the hydrated electron with amino acids, peptides, and proteins in aqueous solution: I. Factors affecting the rate constants. Radiation Research, 62(2), 337-346.

[17] Vasil'ev, Y. V., Figard, B. J., Voinov, V. G., Barofsky, D. F., & Deinzer, M. L. (2006). Resonant electron capture by some amino acids and their methyl esters. Journal of the American Chemical Society, 128(16), 5506-5515.

[18] Nesterov, S. V., Yaguzhinsky, L. S., Podoprigora, G. I., & Nartsissov, Y. R. (2020). Amino acids as regulators of cell metabolism. Biochemistry (Moscow), 85, 393-408.

[19] Bröer, S., & Bröer, A. (2017). Amino acid homeostasis and signalling in mammalian cells and organisms. Biochemical Journal, 474(12), 1935-1963.

[20] Yudkoff, M. (2012). Disorders of amino acid metabolism. In Basic Neurochemistry (pp. 737-754). Academic Press.

[21] Marov, M. Y. (2020). Radiation and space flights safety: an insight. Acta Astronautica, 176, 580-590.

[22] Rizzo, A., Borra, E. M., Ciciani, L., Di Fino, L., Romoli, G., Amantini, G. S., ... & Narici, L. (2023). Foundations of radiological protection in space: the integrated multidisciplinary

approach for next manned missions in deep space. The European Physical Journal Plus, 138(11), 1001.

[23] Zheng, Y., & Sanche, L. (2013). Low energy electrons in nanoscale radiation physics: Relationship to radiosensitization and chemoradiation therapy. Reviews in Nanoscience and Nanotechnology, 2(1), 1-28.

[24] Sanche, L. (2016). Interaction of low energy electrons with DNA: Applications to cancer radiation therapy. Radiation Physics and Chemistry, 128, 36-43.

[25] Verma, P., Narayanan SJ, J., & Dutta, A. K. (2023). Electron attachment to DNA: The protective role of amino acids. The Journal of Physical Chemistry A, 127(10), 2215-2227.

[26] Solomun, T., & Skalický, T. (2008). The interaction of a protein–DNA surface complex with low-energy electrons. Chemical Physics Letters, 453(1-3), 101-104.

[27] Ptasińska, S., Li, Z., Mason, N. J., & Sanche, L. (2010). Damage to amino acid–nucleotide pairs induced by 1 eV electrons. Physical Chemistry Chemical Physics, 12(32), 9367-9372.

[28] Sevilla, M. D. (1970). Radicals formed by electron attachment to peptides. The Journal of Physical Chemistry, 74(18), 3366-3372.

[29] Abdoul-Carime, H., Gohlke, S., & Illenberger, E. (2004). Degradation of N-acetyl tryptophan by low-energy (< 12 eV) electrons. Journal of the American Chemical Society, 126(38), 12158-12161.

[30] Kopyra, J., König-Lehmann, C., & Illenberger, E. (2012). Low energy electron attachment to N-acetyl glycine. Chemical Physics Letters, 550, 47-51.

[31] Kopyra, J. (2012). Electron attachment to the N-substituted amino acids N-methyl glycine and N-methyl alanine: Effective cleavage of the N–Cα bond at sub-excitation energies. Chemical Physics Letters, 533, 87-91.

[32] Muftakhov, M. V., & Shchukin, P. V. (2011). Dissociative electron attachment to glycyl-glycine, glycyl-alanine and alanyl-alanine. Physical Chemistry Chemical Physics, 13(10), 4600-4606.

[33] Gschliesser, D., Vizcaino, V., Probst, M., Scheier, P., & Denifl, S. (2012). Formation and decay of the dehydrogenated parent anion upon electron attachment to dialanine. Chemistry–A European Journal, 18(15), 4613-4619.

[34] Puschnigg, B., Huber, S. E., Probst, M., Tanzer, K., Vizcaino, V., da Silva, F. F., ... & Denifl, S. (2013). Electron attachment to the dipeptide dialanine: influence of methylation on site selective dissociation reactions. Physical Chemistry Chemical Physics, 15(11), 3834-3840.

[35] Kopyra, J., König-Lehmann, C., & Illenberger, E. (2013). Electron attachment to the dipeptide alanyl-glycine. Chemical Physics Letters, 578, 54-58.

[36] Puschnigg, B., Huber, S. E., Scheier, P., Probst, M., & Denifl, S. (2014). Bond cleavage reactions in the tripeptide trialanine upon free electron capture. The European Physical Journal D, 68, 1-6.

[37] Muftakhov, M. V., & Shchukin, P. V. (2014). Resonant dissociative electron capture by simple tripeptides. Russian Chemical Bulletin, 63, 642-650.

[38] Muftakhov, M. V., Shchukin, P. V., & Khatymov, R. V. (2021). Thymidine and stavudine molecules in reactions with low-energy electrons. Radiation Physics and Chemistry, 184, 109464.

[39] Aflatooni, K., Hitt, B., Gallup, G. A., & Burrow, P. D. (2001). Temporary anion states of selected amino acids. The Journal of Chemical Physics, 115(14), 6489-6494.

[40] Sanche, L., & Schulz, G. J. (1972). Electron transmission spectroscopy: Rare gases. Physical Review A, 5(4), 1672.

[41] Jordan, K. D., & Burrow, P. D. (1987). Temporary anion states of polyatomic hydrocarbons. Chemical Reviews, 87(3), 557-588.

[42] Modelli, A. (2003). Electron attachment and intramolecular electron transfer in unsaturated chloroderivatives. Physical Chemistry Chemical Physics, 5(14), 2923-2930.

[43] Scheer, A. M., Mozejko, P., Gallup, G. A., & Burrow, P. D. (2007). Total dissociative electron attachment cross sections of selected amino acids. The Journal of Chemical Physics, 126(17) 174301.

[44] Gallup, G. A., Burrow, P. D., & Fabrikant, I. I. (2009). Electron-induced bond breaking at low energies in HCOOH and glycine: The role of very short-lived σ∗ anion states. Physical Review A, 79(4), 042701.

[45] Abouaf, R. (2008). Low energy electron impact in gas phase glycine, alanine and propanoic acid: Electronic, vibrational excitations and negative ions. Chemical Physics Letters, 451(1-3), 25-30.

[46] Shchukin, P. V., Muftakhov, M. V., Morré, J., Deinzer, M. L., & Vasil'ev, Y. V. (2010). High resolution mass analysis of N-and C-terminal negative ions resulting from resonance electron capture by aliphatic amino acids. The Journal of Chemical Physics, 132(23) 234306.

[47] Gohlke, S., Rosa, A., Illenberger, E., Brüning, F., & Huels, M. A. (2002). Formation of anion fragments from gas-phase glycine by low energy (0–15 eV) electron impact. The Journal of Chemical Physics, 116(23), 10164-10169.

[48] Ptasinska, S., Denifl, S., Abedi, A., Scheier, P., & Märk, T. D. (2003). Dissociative electron attachment to gas-phase glycine. Analytical and Bioanalytical Chemistry, 377, 1115-1119.

[49] Mauracher, A., Denifl, S., Aleem, A., Wendt, N., Zappa, F., Cicman, P., ... & Illenberger, E. (2007). Dissociative electron attachment to gas phase glycine: Exploring the decomposition pathways by mass separation of isobaric fragment anions. Physical Chemistry Chemical Physics, 9(42), 5680-5685.

[50] Ptasińska, S., Denifl, S., Candori, P., Matejcik, S., Scheier, P., & Märk, T. D. (2005). Dissociative electron attachment to gas phase alanine. Chemical Physics Letters, 403(1-3), 107-112.

[51] Vizcaino, V., Bartl, P., Gschliesser, D., Huber, S. E., Probst, M., Märk, T. D., ... & Denifl, S. (2011). Dissociative electron attachment to β-alanine. ChemPhysChem, 12(7), 1272-1279.

[52] Papp, P., Urban, J., Matejčík, Š., Stano, M., & Ingolfsson, O. (2006). Dissociative electron attachment to gas phase valine: a combined experimental and theoretical study. The Journal of Chemical Physics, 125(20) 204301.

[53] Denifl, S., Flosadóttir, H. D., Edtbauer, A., Ingólfsson, O., Märk, T. D., & Scheier, P. (2010). A detailed study on the decomposition pathways of the amino acid valine upon dissociative electron attachment. The European Physical Journal D, 60(1), 37-44.

[54] Matejčík, Š., Kočíšek, J., Kubala, D., Stano, M., & Ingolfsson, O. (2006, December). Gas Phase Dissociative electron attachment study to L-Valine. In AIP Conference Proceedings (Vol. 876, No. 1, pp. 117-124). American Institute of Physics.

[55] Papp, P., Shchukin, P., & Matejčík, Š. (2010). Specific formation of negative ions from leucine and isoleucine molecules. The Journal of Chemical Physics, 132(1) 014301.

[56] Abdoul-Carime, H., König-Lehmann, C., Kopyra, J., Farizon, B., Farizon, M., & Illenberger, E. (2009). Dissociative electron attachment to amino-acids: The case of Leucine. Chemical Physics Letters, 477(4-6), 245-248.

[57] Garattini, S. (2000). Glutamic acid, twenty years later. The Journal of Nutrition, 130(4), 901S-909S.

[58] Johnson, J. L. (1972). Glutamic acid as a synaptic transmitter in the nervous system. A review. Brain Research, 37(1), 1-19.

[59] Maslova, O. V., Senko, O. V., & Efremenko, E. N. (2018). Aspartic and glutamic acids polymers: preparation and applications in medicinal chemistry and pharmaceutics. Russian Chemical Bulletin, 67, 614-623.

[60] Zavilopulo, A. N., & Bulhakova, A. I. (2019). Mass spectrometry of glutamic acid and glutamine in the gas phase. Technical Physics Letters, 45(12), 1252-1257.

[61] Zavilopulo, A. M., Demes, S., Remeta, E. Y., & Bulhakova, A. I. (2021). Electron-impact ionization of the glutamic acid and glutamine molecules. Ukrainian Journal of Physics, 66(9), 745.

[62] Dos Santos, K., Bertho, G., Baudin, M., & Giraud, N. (2024). Glutamine: A key player in human metabolism as revealed by hyperpolarized magnetic resonance. Progress in Nuclear Magnetic Resonance Spectroscopy 144–145 (2024) 15–39

[63] Alizadeh, E., Chakraborty, D., & Ptasińska, S. (2022). Low-energy electron generation for biomolecular damage inquiry: Instrumentation and methods. Biophysica, 2(4), 475-497.

[64] Beerlage, M. J. M., Farago, P. S., & Van der Wiel, M. J. (1981). A search for spin effects in low-energy electron scattering from optically active camphor. Journal of Physics B: Atomic and Molecular Physics, 14(17), 3245.

[65] Campbell, D. M., & Farago, P. S. (1985). Spin-dependent electron scattering from optically active molecules. Nature, 318(6041), 52-53.

[66] Trantham, K. W., Johnston, M. E., & Gay, T. J. (1995). Failure to observe electron circular dichroism in camphor. Journal of Physics B: Atomic, Molecular and Optical Physics, 28(17), L543.

[67] Dreiling, J. M., & Gay, T. J. (2014). Chirally sensitive electron-induced molecular breakup and the Vester-Ulbricht hypothesis. Physical Review Letters, 113(11), 118103.

[68] Dreiling, J. M., Lewis, F. W., Mills, J. D., & Gay, T. J. (2016). Anomalously large chiral sensitivity in the dissociative electron attachment of 10-iodocamphor. Physical Review Letters, 116(9), 093201.

[69] Dreiling, J. M., Lewis, F. W., & Gay, T. J. (2018). Spin-polarized electron transmission through chiral halocamphor molecules. Journal of Physics B: Atomic, Molecular and Optical Physics, 51(21), 21LT01.

[70] Danger, G., Plasson, R., & Pascal, R. (2012). Pathways for the formation and evolution of peptides in prebiotic environments. Chemical Society Reviews, 41(16), 5416-5429.

[71] Frenkel-Pinter, M., Samanta, M., Ashkenasy, G., & Leman, L. J. (2020). Prebiotic peptides: Molecular hubs in the origin of life. Chemical Reviews, 120(11), 4707-4765.

[72] Glavin, D. P., Burton, A. S., Elsila, J. E., Aponte, J. C., & Dworkin, J. P. (2019). The search for chiral asymmetry as a potential biosignature in our solar system. Chemical Reviews, 120(11), 4660-4689.

[73] Barron, L. D. (2021). Symmetry and chirality: where physics shakes hands with chemistry and biology. Israel Journal of Chemistry, 61(9-10), 517-529.

[74] Johnson, L. N. (2005). Asymmetry at the molecular level in biology. European Review, 13(S2), 77-95.

[75] Pshenichnyuk, S. A., Modelli, A., Jones, D., Lazneva, E. F., & Komolov, A. S. (2017). Low-energy electron interaction with melatonin and related compounds. The Journal of Physical Chemistry B, 121(16), 3965-3974.

[76] Pshenichnyuk, S. A., Asfandiarov, N. L., Vorob'ev, A. S., & Matejčík, Š. (2022). State of the art in dissociative electron attachment spectroscopy and its prospects. Physics-Uspekhi, 65(2), 163.

[77] Pshenichnyuk, S. A., Asfandiarov, N. L., Rakhmeyev, R. G., Safronov, A. M., & Komolov, A. S. (2023). On delicate balance between formation and decay of tetracyanoethylene molecular anion triggered by resonance electron attachment. The Journal of Chemical Physics, 158(16) 164309.

[78] Do, H. T., Chua, Y. Z., Kumar, A., Pabsch, D., Hallermann, M., Zaitsau, D., ... & Held, C. (2020). Melting properties of amino acids and their solubility in water. RSC advances, 10(72), 44205-44215.

[79] Cannington, P. H., & Ham, N. S. (1979). The photoelectron spectra of amino-acids: A survey. Journal of Electron Spectroscopy and Related Phenomena, 15(1), 79-82.

[80] Orient, O. J., & Srivastava, S. K. (1983). Production of O− from CO2 by dissociative electron attachment. Chemical Physics Letters, 96(6), 681-684.

[81] Abdoul-Carime, H., Gohlke, S., & Illenberger, E. (2004). Conversion of amino-acids by electrons at subexcitation energies. Physical Chemistry Chemical Physics, 6(1), 161-164.

[82] M. J. Frisch et al. Gaussian 09, Revision A.02 (Gaussian, Inc., Wallingford CT, 2009).

[83] Simons, J., & Jordan, K. D. (1987). Ab initio electronic structure of anions. Chemical Reviews, 87(3), 535-555.

[84] Staley, S. W., & Strnad, J. T. (1994). Calculation of the energies of pi* negative ion resonance states by the use of Koopmans' theorem. The Journal of Physical Chemistry, 98(1), 116-121.

[85] Chen, D., & Gallup, G. A. (1990). The relationship of the virtual orbitals of self-consistent-field theory to temporary negative ions in electron scattering from molecules. The Journal of Chemical Physics, 93(12), 8893-8901.

[86] Scheer, A. M., & Burrow, P. D. (2006). π* orbital system of alternating phenyl and ethynyl groups: Measurements and calculations. The Journal of Physical Chemistry B, 110(36), 17751-17756.

[87] Barron, L.D. Chirality and Life. Space Sci Rev 135, 187–201 (2008).

[88] Wang, D. Z. (2005). Conservation of helicity and helical character matching in chiral interactions. Chirality, 17(S1), S177-S182.

[89] Wang, D. Z. (2005). Conservation of helical asymmetry in chiral interactions. Tetrahedron, 61(30), 7125-7133.

[90] Burrow, P. D., & Modelli, A. (2013). On the treatment of LUMO energies for their use as descriptors. SAR and QSAR in Environmental Research, 24(8), 647-659.

[91] Burrow, P. D., Gallup, G. A., & Modelli, A. (2008). Are there π* shape resonances in electron scattering from phosphate groups? The Journal of Physical Chemistry A, 112(17), 4106-4113.

[92] Rusetsky, V. S., Golyashov, V. A., Eremeev, S. V., Kustov, D. A., Rusinov, I. P., Shamirzaev, T. S., ... & Tereshchenko, O. E. (2022). New spin-polarized electron source based on alkali antimonide photocathode. Physical Review Letters, 129(16), 166802.

[93] Tereshchenko, O. E., Golyashov, V. A., Rusetsky, V. S., Mironov, A. V., Demin, A. Y., & Aksenov, V. V. (2021). A new imaging concept in spin polarimetry based on the spin-filter effect. Journal of Synchrotron Radiation, 28(3), 864-875.

[94] Golyashov, V. A., Rusetsky, V. S., Shamirzaev, T. S., Dmitriev, D. V., Kislykh, N. V., Mironov, A. V., ... & Tereshchenko, O. E. (2020). Spectral detection of spin-polarized ultra low-energy electrons in semiconductor heterostructures. Ultramicroscopy, 218, 113076.

[95] Tereshchenko, O. E., Golyashov, V. A., Rusetsky, V. S., Kustov, D. A., Mironov, A. V., & Demin, A. Y. (2023). Vacuum Spin LED: First Step towards Vacuum Semiconductor Spintronics. Nanomaterials, 13(3), 422.