Electron Impact-Induced Excitation of Valine Molecules in the Gas Phase

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Abstract—We describe the method of measurements and present the results obtained by optical spectroscopy for the excitation of valine molecules in the gas phase by collisions with low-energy electrons. Emission spectra of the excited molecules were measured in a wavelength interval of 260–440 nm upon excitation with electrons in the energy range of 10–70 eV. For the most intense spectral lines, optical functions of electron impact-induced excitation were measured in an energy range of 3–90 eV.

Keywords: electron impact, valine, excitation, fragmentation.

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Ionizing radiation acting upon a living organism may cause various changes in the genotype through an effect on the genes of DNA and RNA. Penetrating into the organism, this radiation generates flows of low-energy secondary electrons with energies ranging from 0.1 to several dozen electronvolts [1]. Secondary electrons can initiate excitation [2, 3] and ionization [4] processes leading to destructive changes in DNA and RNA molecules [5]. Estimation of the consequences of physical excitation and ionization processes caused by electron impact in biological structures requires gaining information about the most probable channels of fragmentation of biomolecules.

The excitation of molecules by low-energy electrons is accompanied by the transition of one or several electrons in the initial molecule to higher-lying states. The subsequent deexcitation leads to the appearance of emission bands of both the initial molecule and its fragments, as well as spectral lines of separate atoms (e.g., hydrogen) in the emission spectra, involving a wide interval of wavelength from the IR up to the visible and UV ranges [6].

Naturally, optical spectroscopy is the most important method for these investigations, and using monoenergetic electron beams for the excitation of complex molecules in the gas phase allows obtaining information on the positions and structure of energy levels and estimating relative probabilities of excitation processes. Investigation of molecules in the gas phase allows one to exclude the effects of solvation, which can otherwise influence the conformational stability of molecules and redistribution of the vibrational excitation in real bioorganic systems.

According to the commonly accepted notions [7], low-energy electron impact mostly accounts for destructive changes on the molecular level of biostructures, with genetic macromolecules being the main target [8]. Investigation of these processes by various methods, especially for biomolecules, is now of special importance in view of the COVID-19 pandemic [9, 10].

The present work was aimed at studying the emission spectra of valine molecules excited by collisions with low-energy electrons in the gas phase in the energy interval of 10–70 eV, determining the optical-excitation functions (OEFs) for separate emission bands in the energy range of 5–90 eV, and establishing the corresponding excitation mechanisms.

Valine belongs to the group of simple aliphatic nonpolar α-amino acids, contains the largest Cα alkyl side chain, and exists in various conformations. There are two types of isomerism in amino acids: (i) structural isomerism, which is related to features of the carbon skeleton structure and mutual arrangement of functional groups, and (ii) optical (spatial) isomerism. Since α-amino acids contain asymmetric carbon (Cα atom), they can exist in the form of optical isomers (mirror antipodes) that play an important role in the processes of protein biosynthesis.

Figure 1 shows structural schemes of a C5H11NO2 valine molecule. It should be noted that aliphatic amino acids can be considered as model systems for studying the interaction of ionizing radiation and large biomolecules (proteins, peptides). The action of pri-
The flexible carboxyl (–COOH) and amino (–NH₂) functional variability of molecules favors reorientation of the opposite direction. In addition, the conformation of the atom can be oriented either toward the nitrogen or in the vector characteristics [7].

Valine enantiomers possess identical energy characteristics (potentials of excitation and ionization, heats of formation, activation energies) and only differ in their vector characteristics [11]).

As can be seen from Fig. 1, a distinctive feature of valine molecule is the presence of a carbon atom bound to four substituents: (i) a hydrogen atom, (ii) a –COOH carboxyl group, (iii) a –NH₂ amino group capable of attaching the hydrogen ion, and (iv) an alkyl side chain of C₆ atoms, the composition of which determines the main properties of this amino acid. Valine enantiomers possess identical energy characteristics (potentials of excitation and ionization, heats of formation, activation energies) and only differ in their vector characteristics [7].

The carboxyl group can rotate, while the hydrogen atom can be oriented either toward the nitrogen or in the opposite direction. In addition, the conformational variability of molecules favors reorientation of the flexible carboxyl (–COOH) and amino (–NH₂) groups (Fig. 1) with the formation of various intramolecular hydrogen bonds—e.g., those connecting an unshared pair of nitrogen atoms to hydrogen of the hydroxyl group or binding hydrogen of the amino group to oxygen of the carbonyl (NH…O=C) and hydroxyl (NH…OH) groups.

The experiments (described in detail elsewhere [11]) employed a vapor-filled cell in which an ampoule with an independent heater was used to create the necessary concentration (about 6 x 10¹¹ cm⁻³) of valine molecules in the region of interaction with electrons. An electron beam with a 2-mm diameter, current of 10–100 μA, and variable particle energy of 0–90 eV passed via the vapor-filled cell and was detected by a Faraday cup. The degree of electron–beam monoegeticity (full width at half height) was no worse than ΔE₁/₂ = 0.5 eV as automatically determined prior to each measurement. The electron energy for OEF measurements was scanned in a preset interval by automated measurement control system at 100- to 400-meV steps.

Output radiation extracted from the collisional cell via a quartz window in the side wall of vacuum chamber was focused by a lens onto the entrance slit of an MDR–2 diffraction monochromator and detected by a photoelectron multiplier (PEM). The system for automatic control of parameters and registration of the useful signal made it possible to operate in the photon counting mode and send electronic pulses from a photomultiplier for processing and recording on a personal computer. The optical emission spectra were measured in a λ = 260–440 nm interval at a 0.547-nm step. The exposure time of signal accumulation was selected within 1–5 s/point, and the monochromator entrance slit width was set at 1 mm, which ensured a spectral resolution of Δλ = 2 nm.

For correct interpretation of the obtained results, the calibration of energy scale of the exciting electron beam was performed using two independent methods: (i) using the shift of the current–voltage characteristic of electron beam current to collector and (ii) using the excitation threshold of the Hg resonance line at λ = 253.7 nm (Eₘₕ = 4.885 eV) and position of the sharp maximum E = 14.224 eV in the OEF of the N₂ spectral band at λ = 337.1 nm (C²Π₉ → B²Π₉). The drum scale in the wavelengths of the spectral instrument is calibrated by spectral lines of the Hg atom at at λ = 253.7, 334.1, and 365.0 nm. Thus, the uncertainty of the electron energy scale for OEF measurements established by calibration was no worse than ±0.1 eV, while that of the scale of spectral instrument was no worse than ±0.25 nm.

The measurement procedure contained two stages: at the first stage, the emission spectra of valine molecules were recorded for fixed electron energies of 30, 50, and 70 eV in a wavelength interval of 260–440 nm (Fig. 2), and, at the second stage, the OEFs were measured for the most intense emissions including both the molecular bands and atomic lines (Fig. 3).

For an exciting electron energy of Eᵦᵣᵣ = 30 eV, the optical emission spectrum displays two bright bands near 280 and 307 nm and several weak emissions in a longer-wavelength region. An increase in electron energy is accompanied by general growth in the emission intensity. The sharpest increase in intensity is observed for a short-wavelength band at 280 nm,
which begins to dominate in the spectrum. In the long-wavelength region, the most pronounced emission bands are observed at 321, 332, 350, 362.5, 381, 406.5, and 429 nm (Fig. 2).

The complex structure of valine molecule (Fig. 1) and well-known literature data [12] allow only some of the observed molecular emission bands to be identified. In the spectrum recorded for $E_{\text{exc}} = 30$ eV, the
main contribution to emission in a rather wide band at \( \lambda = 307 \) nm is related to the excited OH radical (transition \( A^3\Sigma^+ \rightarrow A^3\Pi \), 0–0 band), the emission of which splits into components at wavelengths of 306.5, 306.8, and 309.2 nm. Deexcitation of this system with vibrational levels 1–1 is manifested at wavelengths \( \lambda = 312.5 + 314.5 \) nm, and the system with vibrational levels 2–2 is effectively manifested at wavelengths \( \lambda = 318.5, 321, \) and 323 nm in agreement with the peaks observed in the spectrum (Fig. 2). In addition, a detailed investigation of the emission spectrum of OH radical [13] makes it possible to also identify transitions in this system with vibrational levels 1–0, which lead to the appearance of bands at \( \lambda = 281.2 \) and 283 nm and the most intense band at \( \lambda = 284 \) nm. It can also be ascertained that the measured spectrum reveals slight manifestation of an emission band in the system \( B^3\Sigma^+ \rightarrow A^3\Sigma^+ \) at \( \lambda = 278.04 \) nm in the form of a short-wavelength “shoulder.” This is by no means surprising, since the minimum excitation energy for the \( A^3\Sigma^+ \) level amounts to 4.052 eV and that for the \( B^3\Sigma^+ \) level is 8.65 eV.

At the same time, it should be noted that the ratio of intensities of the emission bands of OH molecule with vibrational levels 1–0 (283 nm) and 0–0 (307–309 nm) for the other methods of excitation [13] amounted to ~0.37. In our experiments, this ratio was 0.67 for the electron energy of 30 eV, 1.28 for 50 eV, and 1.58 for 70 eV. However, an increase in the energy of impinging electrons must not lead to significant variation of the OEFs for both these molecular emission bands at \( \lambda = 283, 311, \) and 335 nm, as well as for the spectral line \( H_\beta \) of the hydrogen atom (\( \lambda = 486 \) nm). Figure 3 shows an example of OEFs measured for the molecular emission band at \( \lambda = 284 \) nm and the atomic hydrogen spectral line \( H_\beta \) at \( \lambda = 486 \) nm. The excitation energy thresholds determined in our experiments for all these emissions fall within 10–11 eV. Evidently, this very interval contains the energy threshold for the fragmentation of a valine molecule. Growth in the quantum yield with increasing energy of bombarding electrons is individual for each emission (band or line), which is evidence of the informativity of these investigations of the fragmentation process.

In concluding, it should be noted that the investigation of amino acids by means of electron impact in the gas phase provides extensive information on their unique properties and allows determining the thresholds and degrees of fragmentation during interaction with electrons and estimating the parameters of intermolecular bonds.

**CONFLICT OF INTEREST**

The authors declare that they have no conflicts of interest.

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