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# Development of a method for molecular beam mass spectrometry of supersonic jets ionized by a high-voltage electron beam

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A technique for studying the mass spectra of rarefied gases clustered flows using an original combination of two diagnostic tools for supersonic jets: a high-voltage electron beam in a supersonic clustered stream for the ionization of jet particles and molecular beam mass spectrometry of the separated ion stream is proposed. Variants of the measuring system, which provided the possibility of ionization of particles of the flow by electrons of a given energy at an arbitrarily selected section of the supersonic jet are proposed, as well as a unique opportunity to analyze the collision process and energy exchange between ionized and neutral particles under conditions of wide variation in the density of neutral gas (collision frequency) are proposed. The possibilities of the diagnostic system for different gas dynamics of flows are shown. Recommendations on the choice of the nozzle-skimmer distance for various geometric and gas dynamic parameters of the outflow and the optimal gap between the electron beam and the skimmer are presented. The possibilities and advantages of the implemented methodology are demonstrated. The result of empirical optimization of the potentials of the ion transport system is presented. An illustration of the capabilities of the developed method is given..

**Keywords:** molecular beam mass spectrometry, high-voltage electron beam, supersonic jets, clusters.

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## Introduction

Technique of molecular rays formed from supersonic jets of low-density gases using a skimmer has been used for mass spectrometry for many years, starting from pilot works of Kantrowitz and Grey papers [1]. This method, compared to the previously used effusion one [2], made it possible to substantially, by several orders of magnitude, increase the intensity and narrow the function of particle speed distribution in a molecular ray and accordingly expand the circle of the solved experimental tasks. One of the complex problems that arose in the method implementation, was the need to correctly form a molecular ray from a supersonic gas jet with the help of an obstacle−skimmer added to this jet [3–7]. In particular, the selection of the optimal external and internal cone angles of the skimmer [3–5] was justified, the simplicity of the front edge of the skimmer nozzle [6], and also the necessary level of density in the oncoming flow [5,7] compared to the diameter of the input hole of the skimmer, i.e. minimum Knudsen number [4], when skimmer interaction may be neglected.

As vacuum engineering capabilities improve, and vacuum pump capacity increases, it became possible to substantially increase the gas flow rate leaking from a forechamber via a sonic or a supersonic nozzle. Growth of local density, substantial reduction of local temperature in a supersonic jet caused formation of clusters [8–9]. The method of cluster formation in a supersonic flow has become most widely used in the supersonic flow to produce clusters of various types and dimensions. Accordingly, it became necessary to diagnose cluster flows.

One of the most available methods for detection of flows with clusters is mass-spectrometry. In most studies, despite the variety of used types of mass-spectrometers (radio frequency [10], time-of-flight [11], quadrupole [12] and many more), particle masses are determined during ionization of a neutral molecular ray directly in a mass analyzer detector. The main problem of using conventional mass-spectrometers is invasive process of neutral particle ionization, which mostly uses electrons of energies in the range of 40−100 eV. Under conditions of the gas mixture flows, especially in presence of complex molecules in the composition, this problem is exacerbated greatly. Especially complex processes arise in mass spectrometry using electron ionization in flows with condensation, since such ionization causes destruction of Van der Waals clusters and formation of a high number of many hard-to-identify fragments, which prevents collection of valid information on the actual distribution of particle masses in a clustered flow [13]. Usage of photon ionization [14–16] has some complicating moments and will not solve this problem completely. A typical example that illustrates the mass spectrum of a mix of argon with an elemental hydrocarbon — methane as a supersonic jet leaks through a supersonic nozzle in the condensation conditions, at pressure in the nozzle forechamber (stagnation pressure), $P_0 = 300$ kPa, is presented in Fig. 1, borrowed from [17]. Gas flow in this case was activated by internal electronic beam of mass-spectrometer with electron energy 70 eV. Note that in this mode and further in all measurements the temperature in the nozzle forechamber (stagnation temperature) made 298±2 K.

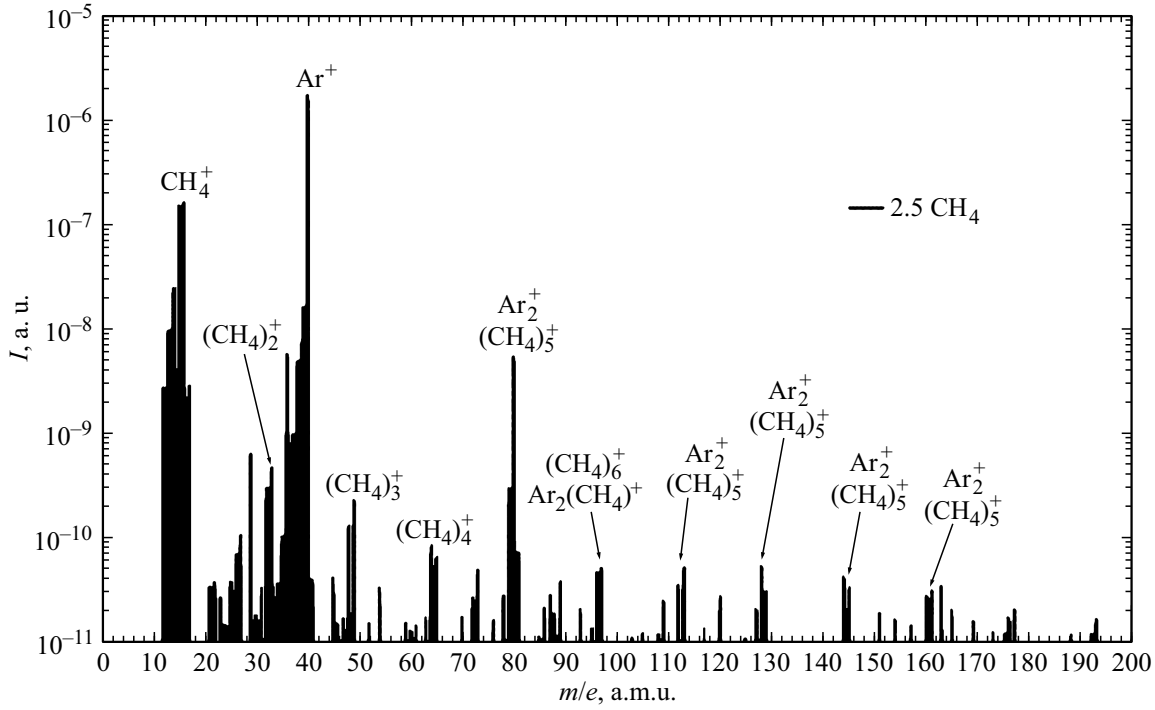


**Figure 1.** Mass-spectrum of argon-methane mix. Braking pressure $P_0 = 300$ kPa.

We will not analyze in detail the produced spectrum, since it is done in the cited paper. We will only note that it was not possible to validly decode all peaks. Besides, you can see that cluster components have considerably lower intensity vs monomers. Therefore, in such measurements the experimenter has to restrict themselves to registration of small size clusters, as a rule, dimers and trimers, less frequently — tetramers.

At the same time the research of cluster generation processes in supersonic jets [18–20] causes the need for obtaining the valid information directly from the field of the supersonic jet area. To measure parameters of supersonic jets, electron-beam diagnostics is widely used [21–26], which is traditionally used for visualization of supersonic flows, measurements of local density and temperature. The authors of this paper also have the corresponding equipment [27,28] and long-term experience of using electron-beam diagnostics in various research, including in clustered flows [29–32]. However, until recently no attempts have been made to use a high-voltage electron beam crossing the supersonic jet in the field upstream the skimmer installed on the axis of the jet as a source of ions for molecular-beam mass-spectrometry.

Let us consider the problems arising in the implementation of such process. Installation of a skimmer in close vicinity to the electronic beam is not realistic, since, as experience has shown, except for a narrow well-focused main beam, a certain number of scattered and secondary electrons is present in the area around it. Exposure to such electrons causes damage of a thin or a sharp skimmer nozzle. Therefore, the skimmer must be forcedly located at a certain distance from the electronic beam in the downward flow direction. In this paper the optimal distance was found experimentally in this paper from the electron beam, which was safe for the skimmer and made to 10 mm. As a result the interval in the jet between the axis of the electronic beam and the inlet cross section of the skimmer becomes the area of collisions of the ionized and neutral particles of the flow. This process of collisional energy exchange only stops inside the skimmer, provided that the necessary Knudsen number is maintained. To minimize the impact of the energy exchange in this jet section, it is feasible to place the electronic beam and the skimmer in the low density area, when particle collisions downstream the electronic beam could be neglected. However, if this area is located further downstream, then, as the previously research shows [33–35], background gas may enter the jet from the environment, which may also add distortions to the recorded parameters of the jet.

The second, but nonetheless important objective is the need to organize transport of ionized particles to the detector of the mass-spectrometer, which is located in the molecular-beam section with the disconnected internal ionization block. The highest complexity in organization of delivery of charged flow particles to the detector of the mass-spectrometer and optimization of the focusing system is the selection of parameters of the focusing lenses. A quite well-readable process for the particles with identical or close mass (traditional models of the accelerating equipment calculation [36,37]), becomes highly complicated in the clustered flow, when the masses of particles may differ by several orders of magnitude. Therefore, selection of

the conditions for transport of ions via the molecular-beam system becomes an empirical problem.

There are more objectives and problems. First of all, this is potential destruction of some clusters in the electron beam. This problem considered in many studies both in our country and abroad (see, for example, [38–43]), is still among the challenging ones. Theoretical modeling of processes for interaction of electrons of various energies with clusters of different, mostly large, size is complicated by a huge number of elementary processes with unknown constants. Experiments with large clusters are limited by a dynamic range of mass-spectrometers, and by difficulty to differentiate fragments of clusters produced from collisions with electrons, from clusters that are not subjected to destruction. Besides, share of condensate in a supersonic flow is usually limited to 10–30% of the total number of particles, as a result of which the exceptionally large range of mass-spectrometer sensitivity is required to record the entire distribution of particles by size. In this paper, if you have a mass-spectrometer with mass range from 1 to 1000, it is currently unreal to solve the problem of cluster destruction under exposure to the high-voltage electron beam. Probably, the approach to solving such a problem will be found in the future when the capabilities of the ionization molecular-beam mass-spectrometry are combined with laser spectroscopy of Raleigh scattering [44,45].

On the other hand, research of collisional processes between ionized, excited and neutral particles with account of the possibility to adjust the conditions for interaction by variation of a gas grade, flowing conditions (braking parameters, dimensions and form of nozzles etc.), of electron energy is apparent interest. Therefore, implementation of the proposed method, despite some problems, is feasible for both practical applications and from the point of view of fundamental research.

Therefore, this paper considered the objective of uniting the conventional methods of electron-beam diagnostics and molecular-beam mass-spectrometry to study the processes happening in a clustered supersonic flow ionized with electrons having energy of several keV, by collection and processing of information withdrawn directly from the area of interaction. Solution to this problem includes creation of a work area for experimental modeling of cluster ionization processes using a high-voltage electron beam, analysis of the possibility of collisional energy exchange between cluster ions and neutral particles in the rarefied environment, ensuring subsequent non-collisional transport of atom, molecular and cluster ions to a mass-spectrometer, and illustration of method capabilities using examples.

## 1. Description of the experimental equipment

Experimental works were carried out on a gas dynamic bench LEMPUS-2 of the applied physics department of the Novosibirsk State University described in detail in [28].

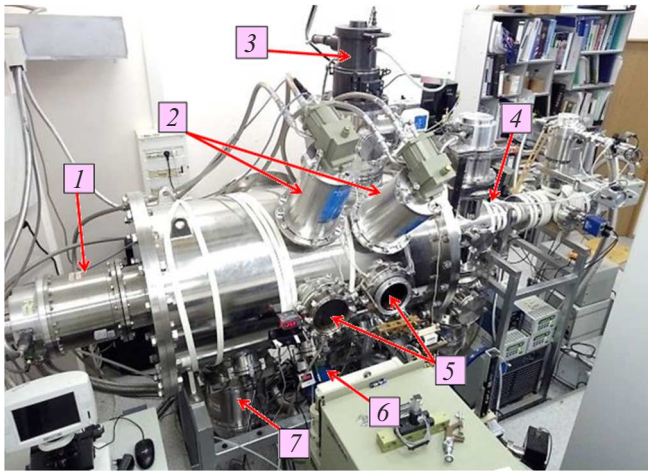


**Figure 2.** Photograph of LEMPUS-2 bench. *1* — additional turbomolecular pump, *2* — additional helium cryogenic pumps, *3* — source of electrons, *4* — sections of molecular-beam system, *5* — optical tract windows, *6* — main helium cryogenic pump, *7* — main booster turbomolecular pump.

Formation of clusters in a gas flow requires triple collisions, maintenance of which is implemented in the high density supersonic jet. Accordingly, use of such jets causes higher flow rate of leaking gas and higher load at the vacuum pumping system, which limits the range of potential gas flow rates. Therefore, in addition to the vacuum pumping equipment given in [28], the bench was equipped with the second booster turbomolecular pump of high capacity and two additional helium cryogenic pumps, which increased the speed of chamber pumping to $\sim 9000\,l$/s in the range of residual pressure from $10^{-4}$ to $10^{-1}$ Pa. Photograph of LEMPUS-2 bench with upgraded system of high-vacuum pumping is shown in Fig. 2 (top view of the bench from the optical tract side).

The flow circuit diagram of the new method is shown in Fig. 3. The conventional scheme of electron beam diagnostics was combined with another conventional scheme - scheme of molecular beam mass-spectrometry. Electron beam diagnostics here comprises a high voltage electron beam *1*, emitted from a source of electrons with hollow cathode *2*, placed in its own vacuum section *3*. The electron beam crosses the axis of the supersonic jet *4*, leaking from a gas source *5* to a large vacuum volume of the expansion chamber *6* and is collected by an electron collector *7*. The scheme of the molecular beam mass-spectrometry, starting from the skimmer *8*, provides for generation of a molecular beam *9*, passing via the post-skimmer section pumped to deep vacuum *10*, a collimating membrane *11* and superhigh vacuum detector section *12*. Finally the molecular beam reaches the inlet aperture of the detecting head *13* in quadrupole mass-spectrometer Hiden Analytical EPIC1000.

The feature of this scheme is the possibility of mass-spectrometry of the supersonic flow composition both in the traditional scheme using its own ionizer of mass-

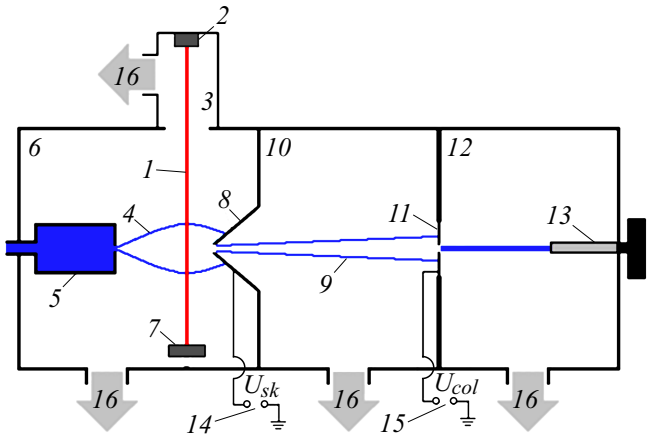


**Figure 3.** Flow circuit diagram of the method: *1* — electron beam, *2* — source of electrons, *3* — electron beam section, *4* — supersonic gas jet, *5* — forechamber with nozzle, *6* — expansion chamber, *7* — electron collector, *8* — skimmer, *9* — molecular beam, *10* — post-skimmer section, *11* — collimator, *12* — detector section, *13* — quadrupole detector of mass-spectrometer, *14, 15* — source of voltage on skimmer $U_{sk}$ and on collimator $U_{col}$, *16* — to vacuum pumps.

spectrometer with low energy electron beam — EBMS option (electron beam mass-spectrometry), and with the connected high voltage electron beam in the expansion chamber with the disconnected own ionization unit of the mass-spectrometer — HVEB option (high voltage electron beam).

Use of the proposed measurement scheme has some advantages that are important to study the clustered supersonic jets, such as the ability to vary the electron energy, making it possible to identify the impact of the ionization process at the recorded mass spectrum; in HVEB version the area of local ionization of gas flow may be provided practically in any area of the jet, which is not permissible in EBMS modes, since for minimization of the skimmer interaction impact it becomes necessary to provide for large distance between the nozzle and the skimmer; it is also permissible to vary time between ionization and detection of ion components of the flow, which provides a unique opportunity to analyze the process of collisions and energy exchange between the ionized and neutral particles under the conditions of variation within the wide limits of the neutral gas density (frequency of collisions). It also becomes possible to compare mass spectra obtained in two versions of flow ionization, making it possible to assess the conditions, when it is feasible to use a certain method.

However, some problems arise on the way of method implementation: probable distortion of the ion composition when ions are transported to the detector, including ion scattering not only in the jet upstream the skimmer but also in the molecular beam; absence of localization of the area for selection of ionized jet particles to the skimmer under the conditions of non-uniformity of the transverse density field in the jet; wide range of cluster sizes. This paper considers and proposes the versions to solve the arising problems.

## 2. Selection of optimal conditions for measurements

To eliminate the impact of the gas dynamic processes of skimmer interaction at sampling from the zone of interest in the supersonic jet, it is necessary to ensure the local Knudsen number at the inlet cut of the skimmer, $\mathrm{Kn}_s > 1$ [4]. Since whenever jets flow out of supersonic nozzles under the conditions of condensation the estimate of $\mathrm{Kn}_s$ is a priori complicated, this paper for several different nozzles, parameters of which are given in Table 1, completed the experimental selection of the skimmer position in jets with different mean number of particles in the cluster, when the skimmer interaction may be neglected. As an example, Fig. 4 shows the results of amplitude measurement for monomers, dimers and trimers of argon depending on the distance from nozzle № 1 at different values of stagnation pressure. Flowing parameters are available in Table 1. Measurements were carried out using the conventional ionization scheme — in the mass spectrometer detector (HVEB version). The average size of clusters is calculated using equations proposed in [46].

Dependences of density on the molecular beam axis on conditions in the supersonic jet are well known. With the fixed geometry of the molecular-beam system, the density on the axis of the molecular beam $n_b$ depends on the density in the supersonic flow at inlet cut of the skimmer $n_s$ and on the squared speed ratio S [47,48]:

$$n_b \sim n_s \cdot S^2,$$

where $S = \frac{W}{\sqrt{2 \cdot k \cdot T/m}}$, $W$ — directed (otherwise — hydrodynamic) flow speed, $k$ — Boltzmann constant, $T$ — temperature, $m$ — particle mass. Note that the value of the

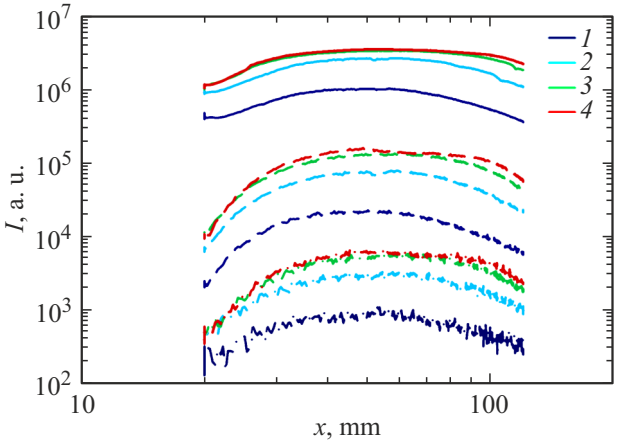


**Figure 4.** Longitudinal profile of supersonic jet for monomers (solid line), dimers (dashed line) and trimers (dash-and-dot line) of argon. Supersonic nozzle № 1, $d^* = 0.18$ mm. Braking pressure: *1* — 150, *2* — 200, *3* — 300, *4* — 400 kPa.

**Table 1.** Parameters of supersonic jet flow from supersonic and sonic nozzles

| № of mode | Stagnation pressure, $P_0$ | Pressure of background gas, $P_\infty$ | $\sqrt{P_0/P_\infty}$ | Average cluster size, $N_{cl}$, Ar, [46] | | | |
|---|---|---|---|---|---|---|---|
| | | | | Nozzle № 1 (supersonic), $d^* = 0.18$ mm $D_a = 2.55$ mm $M_a = 14.7$ | Nozzle № 2 (supersonic), $d^* = 0.24$ mm $D_a = 3.0$ mm $M_a = 13.5$ | Nozzle № 3 (supersonic), $d^* = 0.21$ mm $D_a = 3.5$ mm $M_a = 16.5$ | Nozzle № 4 (sonic), $d^* = 0.505$ mm |
| | kPa | Pa | | Particles in cluster | Particles in cluster | Particles in cluster | Particles in cluster |
| 1 | 50 | 0.25 | 447 | 15 | < 5 | 35 | 7 |
| 2 | 150 | 0.41 | 605 | 94 | 29 | 377 | 44 |
| 3 | 200 | 0.49 | 639 | 233 | 46 | 741 | 79 |
| 4 | 300 | 0.67 | 669 | 603 | 90 | 1921 | 204 |
| 5 | 400 | 0.85 | 686 | 1186 | 219 | 3777 | 401 |

Note. $d^*$ — diameter of critical cross section of nozzle, $D_a$ — diameter of outlet cross section of nozzle, $M_a$ — Mach number at outlet cross section of nozzle.

speed ratio, i.e. ratio of the directed flow speed to the most probable speed of chaotic motion of molecules, is $(\gamma/2)^{0.5}$ lower than the corresponding Mach number (where $\gamma$ — ratio of heat capacities for single-atom gas $\gamma = 5/3$).

As the skimmer moves away from the nozzle, the amplitude of signals on the axis of the molecular beam grows as a result of gradual weakening of the skimmer interaction and growth of speed ratio, despite decreasing density in the supersonic flow. After the weakening of the influence from the jet interaction with the skimmer and moderation of the speed ratio growth, the dominant would be density drop in the jet (inversely proportionate to the squared distance). This result has certain features caused by different average size of clusters formed in the jet at various stagnation pressures, and is specific both for monomers and small clusters, whose dependences are shown in Fig. 4.

The optimal for sampling using the skimmer is the signal of maximum amplitude, but with minimum skimmer impact. According to charts shown in Fig. 4, for nozzle № 1 it is $x = 55 \pm 10$ mm. It is evident that physical dimensions of jets depending on the braking parameters and geometry of supersonic nozzles, vary. Therefore, this value is optimal only for the used range of gas dynamic parameters of the flow and claims no versatility. The similar method was used to determine optimal distances nozzle–skimmer for all nozzles and gas mixtures used in the paper (nozzle № 2 — $40 \pm 10$ mm; nozzle № 3 — $45 \pm 10$ mm; nozzle № 4 — $40 \pm 10$ mm).

Further search for optimal modes was carried out in HVEB version with energy of high voltage beam electrons$E_{eb} = 10$ keV. Let us consider in detail the issue of distance selection between the electron beam and the skimmer, $L_{eb-sk}$. The evident desire to place the skimmer nozzle in the area of the electron beam for instant (momentary) selection of ionized particles in the molecular beam is not feasible, as it was noted above, due to high energy of electrons, capable of evaporating the sharp edge of the skimmer. At the same time increase or variation of distance $L_{eb-sk}$ for research purposes were not included in the objectives of this paper. Therefore, the skimmer was installed at the minimum possible distance from electron beam. The visible diameter of the primary electron beam was usually around 1 mm. However, the glowing halo around the main ray of the electron beam indicates the presence of quite many scatted and secondary electrons around the primary beam. As a rule, these electrons may not introduce noticeable distortions in measurements of density or population of rotational levels of molecules due to their small share, however, their energy is quite sufficient to heat and even melt the sharp front edge of the skimmer. Besides, there is a nonzero probability of spontaneous short-term failure of the focusing system in the used electronic optics, as a result the electronic beam for a short period of time may defocus to the width of more than 10 mm in diameter. Loss of one of deficit skimmers caused the authors to not place the front edge of the skimmer closer than 10 mm from the electron beam axis as a precaution. As a result, the minimum possible size $L_{eb-sk} = 10$ mm was chosen, which makes from 20 to 55 calibers for various diameters of critical cross section of nozzles used in operation. Note that for a supersonic jet with critical diameter of of 0.18 mm (Table 1), for example, at the distance of around 50 mm from the outlet cut of the nozzle, i.e. in $\sim 275$ calibers, the drop of the local density in section 10 mm would make $\sim 40–50\%$.

Estimates of the number of collisions in section $L_{eb-sk}$ between particles of various grade (neutrals, ions, monomers, clusters) as argon leaks via the supersonic nozzle № 1 for various stagnation pressures (50–400 kPa) are given in Table 2. The results are obtained based on the presumption of probability of the formation of ionized particles under exposure to high voltage electron beam of approximately 0.01–0.1% with cluster share in the flow of not more than 20–30%. Limitation of the share of clusters in the flow is caused by the fact that formation of dimers requires triple collisions, as a result of which one of colliding particles

**Table 2.** Number of collisions in section $L_{eb-sk}$ between particles of different grade as argon leaks via a supersonic jet № 1

| $P_0$, kPa | Ion | Neutral particle | |
|---|---|---|---|
| | | Monomer | Cluster |
| 150 | Cluster | 4 | 1 |
| 200 | Cluster | 12 | 5 |
| 300 | Cluster | 24 | 10 |
| 400 | Cluster | 74 | 32 |

captures energy excess, and the remaining two are united in a cluster [49]. Selection of the ionization probability value depends on the results of experiments for measurement of the ratio of ion current in the jet after ionization to the electron beam current [22,25,27]. Density data in section $L_{eb-sk}$ are taken from the theoretical (isentropic) estimate. Since density profiles in the supersonic jets in presence of condensation are below the isentropic dependence, the given estimates produce knowingly higher values taken as the upper limit of the collision number. According to the completed estimates, despite the fact that the speed of ion motion to the skimmer substantially exceeds the speed of neutral particles, collisions of any monomer and cluster ions, any particles at pressures below 150 kPa, and also neutral and ionized monomers between each other and neutral clusters in section $L_{eb-sk}$, may be neglected. Possible number of collisions for other conditions is given in Table 2. Therefore, the proposed version of skimmer location downstream the electron beam brings no substantial distortions to recorded processes.

Since the available programs for optimization of charged particles in electric or magnetic fields [36,37] are not applicable in the conditions of the difference by two and more orders of selected ion masses, the optimality of the conditions for selection of ions using electrical field was checked experimentally. For this purpose controlled potential was supplied to the skimmer, and Faraday cylinder was installed in the post-skimmer section, providing for registration of ions in the near-axial area of the molecular beam. For positively charged ions the change of the accelerating voltage on the skimmer was limited by the following causes. First, the negative potential on the skimmer influenced the electronic beam, especially that the charge inside „cord“ of electrons was not compensated. Therefore, increase of the voltage in the skimmer causes deviation of the electronic beam upstream. Second, the level of background pressure in experiments promoted microcharges on the skimmer and breakthroughs between the skimmer and the grounded elements of the structures inside the expansion chamber. Therefore, in this paper the voltage on the skimmer did not rise above −70 V.

Dependences of ion current $I_{cyl}$ on Faraday cylinder on voltage on skimmer $U_{sk}$ in the range from 0 to −70 V with several supersonic nozzles and at stagnation pressure

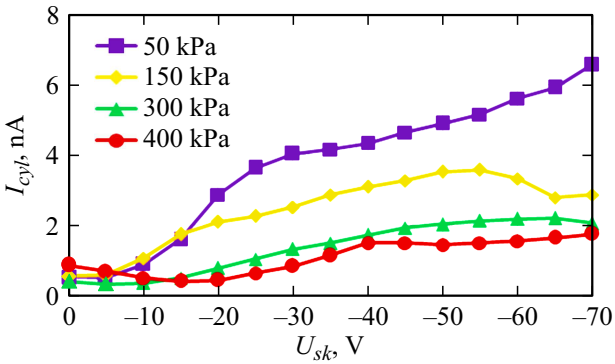


**Figure 5.** Dependence of ion current in molecular beam on potential on skimmer. Argon, supersonic nozzle № 2, $d^* = 0.24$ mm, $M_a = 13.5$.

variation with corresponding variation of the average size of clusters are given in Fig. 5 for nozzle № 2 (Table 1). Analysis of the obtained results, demonstrating high experimental spread of data, nevertheless found the main trends: increased ion current with growth of the negative pressure on the skimmer and reduction of the ion signal with growth of the stagnation pressure and accordingly the average size of clusters in the jet. The logical explanation to the established dependences is the weakened impact of the focusing exposure from electric field to ions of larger mass with account of dominance of heavy clusters near the flow axis. However, it is evident that the process is rather complicated. For further research the potential value on the skimmer was chosen, for which the maximum ion current was observed for most stagnation pressures. Since the highest current of ions for stagnation pressures 150, 300 and 400 kPa is observed in the range of values $|U_{sk}| = 50-55$ V, value $U_{sk} = -50$ V was selected with the purpose to minimize the probability of breakthroughs on the skimmer. It should be emphasized that the objective to focus the flow of ions made of particles with mass differing by orders of magnitude, and also distributed in the space inside and outside of the supersonic jet, is quite complicated even in the case of solving the problem of charge accumulation on the skimmer surface. As noted above, the attempt to use the gained experience in methods of charged particle focusing in accelerators yielded no positive result.

Variation of voltage on the collimator, being an intermediate focusing element in transportation of ions formed in the supersonic jet, to the mass-analyzer of the quadrupole mass-spectrometer, was carried out at selected distances of nozzle-electron beam-skimmer with account of the need to increase the accelerating potential between the skimmer, the collimator and the inlet lattice of the mass-spectrometer analyzer. Fig. 6 shows the example of the produced dependence of the total signal recorded by the mass-spectrometer on the accelerating voltage on the collimator for the argon jet leaking from nozzle № 3 at stagnation pressure $P_0 = 400$ kPa, i.e. in the mode with maximum

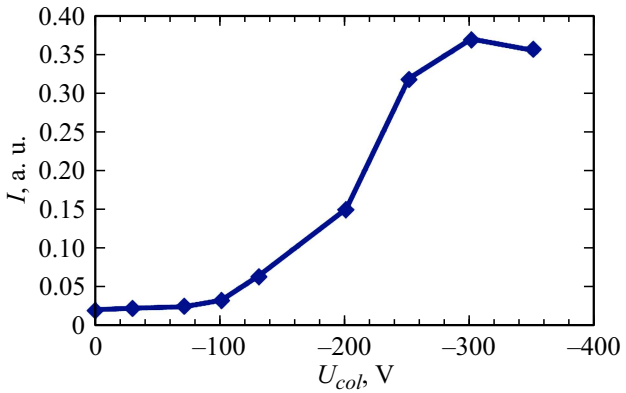


**Figure 6.** Dependence of intensity of the total signal recorded by mass-spectrometer on the potential applied to the collimator. Supersonic nozzle № 3, $d^* = 0.21$ mm, $D_a = 3.5$ mm, $M_a = 16.5$. Potential on skimmer $U_{sk} = -50$ V.

cluster size. Distance between the skimmer and the collimator was 850 mm, between the collimator and inlet aperture of mass analyzer — 500 mm.

As should be expected, the growth of signal amplitude starts at $U_{\text{col}} < -50$ V. At values $U_{\text{col}} < -300$ V the growth of dependence stops due to excess by potential module on the collimator above the potential on the inlet lattice of the mass analyzer. Therefore, in this version of HVEB mode, value $U_{\text{col}} = -300$ V was selected for further studies.

Estimates of the ion motion speed and length of ion free path for monomers and clusters are shown in Table 3. Speed estimates are made on the basis of law of conservation of energy for the motion in electric field: $0.5 \cdot m \cdot v_0^2 + q \cdot U_{sk} = 0.5 \cdot m \cdot v^2$, where $v_0$ — speed of directed motion of charged particle at the moment of ionization, $v$ — speed of directed motion of charged particle at the moment of hole passage in the skimmer nozzle, $m$ — mass of moving particle. Free path lengths were estimated on the basis of the estimate for the number of collisions of ions with the background of post-skimmer and detector sections.

Speed of directed motion of neutral argon particles $\sim 550$ m/s. In its turn, the total speed of ions between the electron beam and the skimmer $V_{sk}$, with the selected values of potentials on the skimmer, does not exceed 15 500 m/s for monomers and 740 m/s — for clusters with size of 1000 particles per cluster. In its turn with the selected potential on the collimator the monomer ion reaches speed of $\sim 38\,000$ m/s, and cluster ion — 1320 m/s at cluster size of 1000 particles per cluster.

Here $P_\infty$, $P_{ps}$, $P_{det}$ — pressure of background gas in the expansion chamber, post-skimmer and detector sections, accordingly; $V_{sk}$, $V_{col}$ — speeds acquired by ions at inlet cuts of the skimmer and the collimator accordingly; $\lambda_{ps}$, $\lambda_{det}$ — average length of ion free path in the post-skimmer and detector sections; $\text{Kn}_{ps}$, $\text{Kn}_{det}$ — corresponding Knudsen numbers for ions by specific longitudinal dimensions of these sections.

As it follows from the estimates given in Table 3, the probability of monomer and cluster ion flight on the way from the skimmer to the mass analyzer without collisions is mostly quite high. And only in the post-skimmer section large ion clusters may collide with particles of background gas at maximum loads on the pumping system of this section. Therefore, with the disconnected own ionization unit of the molecular beam in the selected modes of gas flow from nozzles, the data recorded by the mass-spectrometer characterize processes that happened when the electrons of high voltage beam interact with particles of supersonic flow, with account of corrections made on the way of particles transport from the ionization area to the mass-spectrometer detector. The designed system (with the specified limitations) is the alternative method to study the processes happening in the supersonic clustered flows, flowing from nozzles to the rarefied medium.

## 3. Examples of the results of using HVEB method

Please find below several examples of results obtained by doing research in the clustered jets using HVEB method.

Fig. 7 shows comparison of the mass spectrum of argon obtained at the same gas dynamic parameters by both methods — EBMS and HVEB. For measurements, the sonic nozzle with diameter of 0.505 mm was used. Comparison is made at stagnation pressure 100 kPa at distance nozzle–skimmer 40 mm. For convenience of comparison the obtained results in both modes are normalized by the sum of recorded mass peak amplitudes in the entire recorded mass range $(m/e)$. Here you can see that while amplitude of monomers in HVEB mode is 15% lower than in EBMS mode, amplitudes of cluster peaks in the entire recorded range are several times higher. Nevertheless, the expected maximum of amplitude in the area $m/e \sim 1000$ is not registered, even though the estimate of the average size of clusters by [46] gives value $\langle N \rangle = 25$. The picture observed in Fig. 7, as well as analysis of literature data (for example, [19]) makes it possible to presume that higher energy of ionizing electrons reduces efficiency of electron

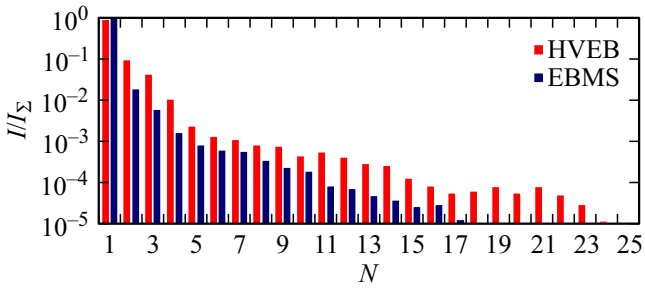


**Figure 7.** Comparison of mass spectra of clustered argon flow normalized by total signal recorded by EBMS method (blue) and HVEB method (red). Braking pressure 100 kPa. Average size of clusters by [46] $\langle N \rangle = 25$. Sonic nozzle № 4, $d^* = 0.505$ mm. $N$ — cluster ion size $(m/e = 40 \cdot \text{N})$.

**Table 3.** Some parameters of argon leaking, estimated for the specified value of the average cluster size in the flow

| $N_{cl}$ part/ cluster | $P_\infty$, Pa | $P_{ps}$, $\mu$Pa | $P_{det}$, $\mu$Pa | $V_{sk}$, km/s | $V_{col}$, km/s | $\lambda_{ps}$, m | $\lambda_{det}$, m | $\mathrm{Kn}_{ps}$ | $\mathrm{Kn}_{det}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | 15.5 | 38.0 | 9.3–26.8 | 209.7–789.8 | 10.9–31.5 | 419.4–1082.5 |
| 5 | 0.3 | 760 | 25.3 | 7.0 | 17.0 | 6.1 | 185.1 | 7.2 | 370.1 |
| 15 | 0.25 | 506.6 | 17.3 | 4.0 | 9.8 | 4.4 | 129.8 | 5.2 | 259.5 |
| 29 | 0.5 | 813.3 | 41.3 | 2.9 | 7.1 | 1.8 | 35.1 | 2.1 | 70.2 |
| 46 | 0.64 | 853.3 | 50.7 | 2.4 | 5.6 | 1.2 | 21.0 | 1.5 | 42.0 |
| 90 | 0.84 | 1053.25 | 60.0 | 1.7 | 4.0 | 0.6 | 11.3 | 0.8 | 22.6 |
| 94 | 0.41 | 733.3 | 33.3 | 1.7 | 3.9 | 0.9 | 19.8 | 1.0 | 39.5 |
| 219 | 1.08 | 1319.9 | 65.3 | 1.2 | 2.6 | 0.3 | 5.7 | 0.3 | 11.4 |
| 233 | 0.5 | 960 | 40 | 1.2 | 2.5 | 0.4 | 8.9 | 0.4 | 17.8 |
| 603 | 0.67 | 1253.2 | 48 | 0.8 | 1.6 | 0.2 | 3.9 | 0.2 | 7.8 |
| 1186 | 0.85 | 1466.5 | 52 | 0.7 | 1.1 | 0.1 | 2.3 | 0.1 | 4.5 |

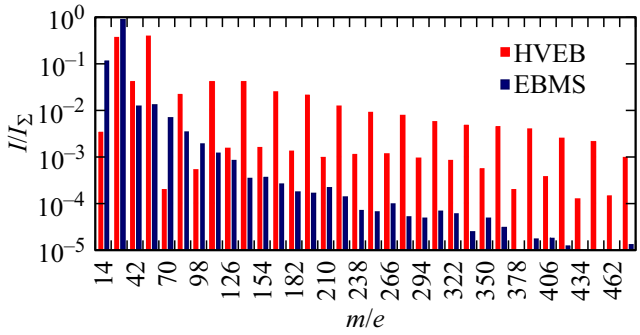


**Figure 8.** Comparison of mass spectra of clustered nitrogen flow normalized by total signal recorded by EBMS method (blue) and HVEB method (red). Pressure in nozzle forechamber is 140 kPa. Average size of clusters by [46] $\langle N \rangle = 40$. Sonic nozzle № 4, $d^* = 0.505$ mm.

interaction with jet particles, including with clusters, and, accordingly, reduces the intensity of cluster disintegration as a result of ionization.

To confirm the above assumption, mass spectra were recorded for the supersonic clustered flow of nitrogen at the same gas dynamic parameters using methods of EBMS and HVEB. These mass spectra normalized for the total intensity of signals are shown in Fig. 8. As you can see, in this chart, as well as in Fig. 7, when recorded by HVEB method, nitrogen monomer peak intensity drops 2.3 times with significant, more than by an order of magnitude, growth of peak intensity at cluster masses of nitrogen. Therefore, the observed result in Fig. 8 confirms the conclusion on the information value of HVEB method to study processes in clustered flows.

Results of experiments for recording of mass spectrum of supersonic clustered flow of argon–hydrogen mix (90%:10%) when the jet is ionized by methods EBMS and HVEB, are shown in Fig. 9, *a*. Fig. 9, *b–d* provides more details on the individual sections of this mass spectrum. For comparison the results in the entire recorded mass range ($m/e$) in both modes are normalized by intensity of the corresponding argon peak ($m/e = 40$). As a result of comparison in Fig. 9, *b* it is established that when HVEB method is used, the relative share of double ionized monomers is almost 3.5 times higher than the result obtained by EBMS method. According to Fig. 9, *c, d*, the relative share of argon dimer and trimer ions increases several times, and intensity of the protonated argon ion peak when recorded by HVEB method in the clustered flow increases by more than an order of magnitude. There is growth of relative intensity of ion peaks in protonated dimers and trimers of argon. This result makes it possible to detect and analyze the processes of argon protonation in the clustered flow, to determine the role of clusters, and also the potential role of collisions of neutral and charged particles in this process downstream from the ionization area.

One of the examples of studies we carried out using HVEB method is the initiation of energy exchange and synthesis of new compounds in the supersonic clustered flow of methane and buffer gas mix. As a result of high difference in amplitudes of monomers, dimers and trimers and other clusters of methane for convenience of analysis Fig. 10 presents a mass spectrum of mix 20%$CH_4$ + 80%He in the mass range $56 < m/e < 1000$, while low mass peaks are shown in Table 4.

A remarkable feature of the given mass spectrum is regular formation of ions $(CH_4)_{q-1}CH_5^+$ $(q = 1, 2, \ldots)$, intensity of which with growth of $m/e$ increases vs the intensity of ions $(CH_4)_q^+$. Further growth $m/e$, at $q > 10$, detects clusters $(CH_4)_{q-2}(CH_5)_2^+$ and even $(CH_4)_{q-3}(CH_5)_3^+$, comparative intensity of peaks of which also increases. Besides, cluster peaks of type $(CH_4)_{q-1}CH^+$ are also formed systematically. It stands to mention the presence of more intense mass peaks compliant with dimensions of clusters 16, 21, 26, 29, 47 and some others vs the surrounding ones, which confirms the presence of more stable connections specific for mass-spectrometry under electron ionization of higher hydrocarbons [50,51]. The given results considerably expanded the range of the

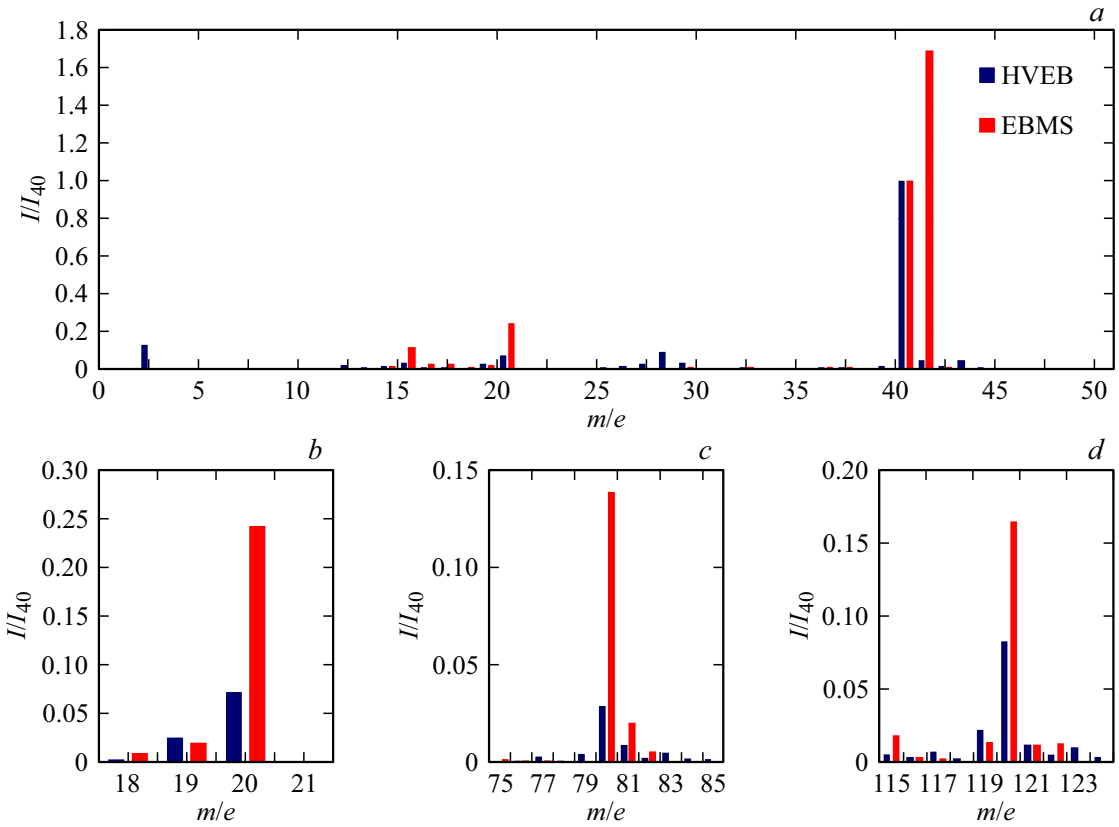


**Figure 9.** Comparison of mass spectra of supersonic flow of gas mixture $Ar + H_2$, recorded by methods of EBMS (blue) and HVEB (red) and built with normalization on argon peak ($m/e = 40$). Supersonic nozzle № 1. Braking pressure 100 kPa. Distance of nozzle–skimmer is 30 mm.

**Table 4.** Intensity of mass spectrum peaks in mix $20\%CH_4 + 80\%He$ for some masses $m/e < 56$

| $m/e$ | 12 | 13 | 14 | 15 | 16 | 32 | 48 |
|---|---|---|---|---|---|---|---|
| $I$, a.u. | $2.2 \cdot 10^5$ | $5.0 \cdot 10^5$ | $6.6 \cdot 10^5$ | $1.9 \cdot 10^6$ | $5.6 \cdot 10^6$ | $2.8 \cdot 10^5$ | $2.2 \cdot 10^4$ |

recorded cluster peaks vs similar data obtained by EBMS method [52]. Therefore, the given examples of using HVEB method illustrate wider opportunities of the method for analysis of the mass composition of clustered molecular beams.

Apart from development of the works illustrated using the given examples, let us form some new objectives that may be investigated using the option of ionization directly in the supersonic jet, and also studied by comparison of two used methods. First, it is absolutely evident that the high voltage electron beam heats jet gas [22]. In the conventional electron beam diagnostics such heating is usually not taken into account, since the life times of excited particles are small compared to the time between collisions in the local diagnosed volume [24]. In case of HVEB the process of collisions in the range between the electron beam and skimmer is unavoidable even when (as it was specified above) the distance nozzle–skimmer increases to the maximum. This makes it possible to investigate such process. Second, as our measurements show [53,54], life times of excited clusters may be much longer than in monomers. This issue, which was many times discussed in literature [19,55], may also be studied when HVEB is used, in particular, when searching for the conditions to convert light hydrocarbons [30]. Third, according to papers [56–58], introduction of electronic beam in the supersonic flow may initiate electron-stimulated condensation, the study of which is also of certain interest.

## Conclusion

Within the framework of this paper, the method is proposed and tested using the capabilities of the conventional high voltage electron beam technique in a combination with molecular beam mass-spectrometry for diagnostics of the process of ionization and destruction of clustered supersonic flows. Until recently no attempts have been made to

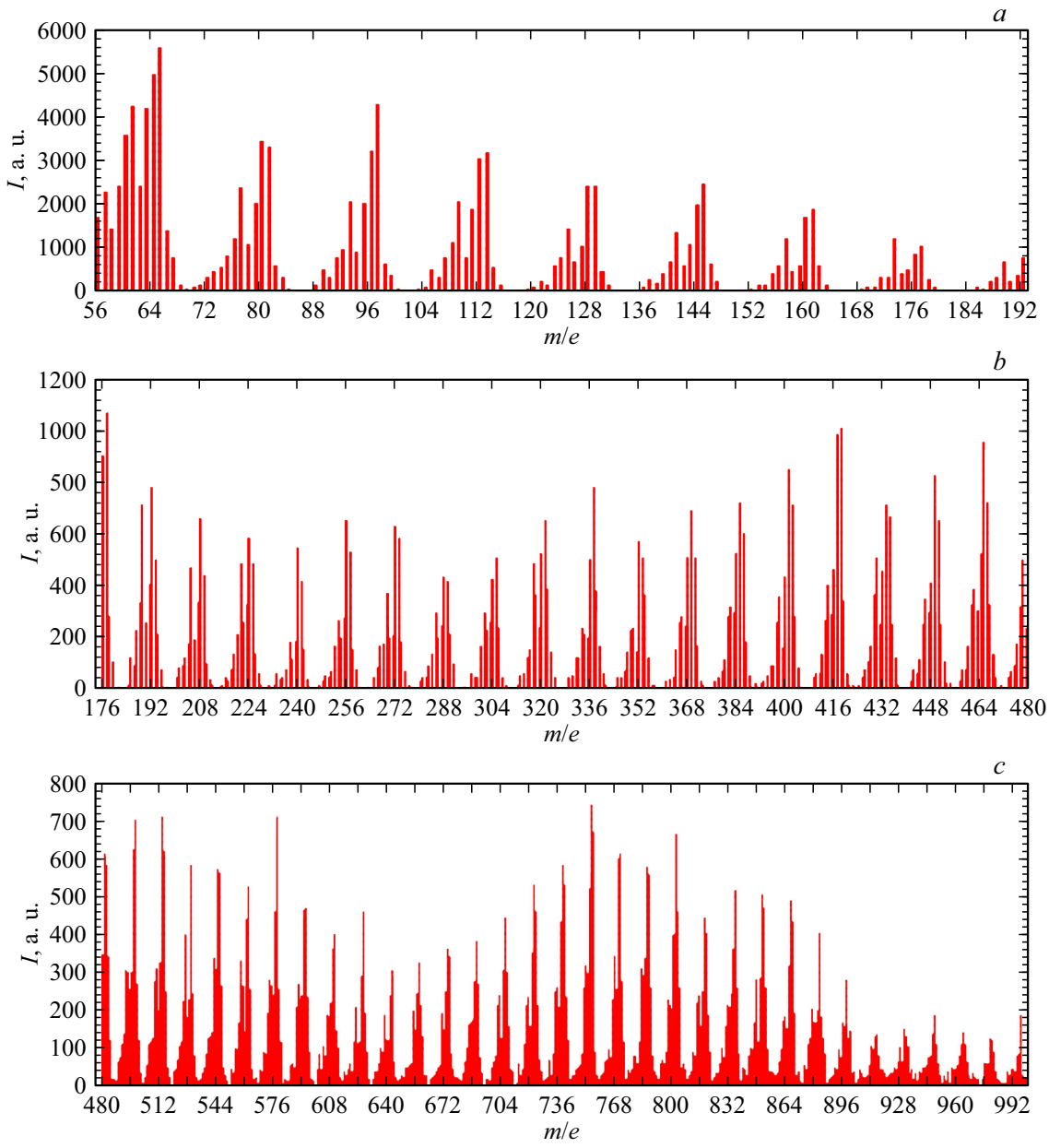


**Figure 10.** Mass spectrum in mix 20%$CH_4$ + 80%He in mass range: *a* — $56 < m/e < 192$; *b* — $176 < m/e < 480$; *c* — $480 < m/e < 1000$. Measurement method — HVEB. Supersonic nozzle № 1. Braking pressure 300 kPa. Distance of nozzle–skimmer 40 mm.

use HVEB crossing the supersonic jet in the field upstream the skimmer installed on the axis of the jet as a source of ions for molecular-beam mass-spectrometry. The created working section for the experimental modeling of the ionization processes in HVEB clusters with their subsequent transport to the mass-spectrometer with the disconnected own ionization unit provided for the expansion of the interval for recorded mass peaks of cluster particles within the limits of the dynamic range of the used mass-spectrometer. Conditions were found that made it possible to minimize the impact of the skimmer interaction, the background gas penetration in the supersonic jet from the environment, and collisional processes in the gap between the electron beam and the skimmer at the measurement results. As a result of the obtained experience, recommendations were given to select the optimal distances between the nozzle, electron beam ans skimmer, the specific values of distances are presented for the used structures of the nozzles and the range of the implemented gas dynamic parameters of the system. Parameters of the ion optics were defined experimentally (potentials supplied to the skimmer and the collimator), providing for the acceptable conditions of ionized particles transport to the detector of the mass-spectrometer in the system of skimmer–collimator–detector. For the skimmer it is $U_{sk} = -50$ V, for the collimator — $U_{col} = -300$ V. It was found that in most implemented modes of jet leaking

and the presented set of nozzles, the collisions between cluster ions and neutral particles in the gap between the electron beam and skimmer, and also in the process of ionized particles motion in the molecular beam, may be neglected.

When results are compared, which were obtained by two methods — conventional and the proposed new one, it is shown that the proposed method of HVEB ionization directly in the supersonic jet upstream the skimmer of the molecular beam system provides for higher sensitivity in recording of cluster ions in the entire dynamic range of the used quadrupole mass-spectrometer as in variation of braking parameters for several nozzle versions, and in the research of the non-ordinary process of argon protonation in mixture of argon−hydrogen. Results of recorded $ArH^+$ and $Ar_2H^+$ ions are shown. The example is given on how to use the finalized method to analyze the process of methane-hydrocarbon mix clustering. A remarkable feature of the recorded mass spectra was regular formation of ions $(CH_4)_{q-1}CH_5^+$ $(q = 1, 2, \ldots)$, intensity of which with growth of m/e increased compared to the intensity of ions $(CH_4)_q^+$. Further growth $m/e$, at $q > 10$ detects clusters $(CH_4)_{q-2}(CH_5)_2^+$ and even $(CH_4)_{q-3}(CH_5)_3^+$, comparative intensity of peaks in which also increased. Besides, cluster peaks of type $(CH_4)_{q-1}CH^+$ were also recorded systematically. Finally, new problems were formulated, which may be promising areas of research using the finalized method.

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### Conflict of interest

The authors declare that they have no conflict of interest.

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