Generation of a low-temperature plasma in a nozzle to initiate ion-cluster reactions in jets of mixtures of methane with a buffer gas

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Abstract. We have considered the option of generating cluster ions directly at the nozzle by initiating an electric discharge. Here, a low-temperature plasma in the flow is formed as a result of the outflow of a partially ionized gas. Conditions for the formation of clusters in the presence of excited particles are provided downstream. To implement this generation option, a scheme for creating an effective discharge in the diffuser part of a supersonic nozzle was proposed and implemented. The diagnostic system of the LEMPUS-2 gas-dynamic facility was adapted to register processes in a supersonic flow of ionized gas with clusters. Molecular nitrogen, which is weakly condensing under experimental conditions, was used as the primary reference gas. The methods of molecular beam mass spectrometry were used to study gas mixtures consisting of 20% methane in an inert carrier gas. Highly condensable argon and practically non-condensable helium were used as carrier gases. It was found that when using the ionized particle selection system for detection, only methane monomers and dimers are registered in mixtures with argon, whereas in mixtures with helium larger clusters are registered. A version of the explanation of the detected dependencies was presented.

1 Introduction

Cluster beams are widely used to form thin films, clean and polish surfaces, and form new particles and materials. A widely used method for generating cluster beams today is the formation of clusters in a supersonic jet of gas or a gas mixture expanding into a rarefied space [1–2]. The popularity of the method is due to the high speed of cluster generation and the possibility of their delivery to the application area. Depending on the outflowing gas or gas mixture, the gas-dynamic parameters of the outflow, and the geometrical parameters of the sonic or supersonic nozzle, the proportion of condensate can reach 20–30% of the total volume of the outflowing gas, and the cluster size can vary from two to thousands of particles.

This method of cluster generation was used by us in [3] to search for conditions for the initiation of ion-molecular reactions in clusters, as well as in [4] in the formation of cluster ions in supersonic jets of methane and its mixtures with inert gases using a high-voltage electron beam crossing the supersonic jet in the selected section. Thus, we tried to implement a variant of the process in the form: first, the formation of clusters, and then their excitation and ionization to initiate the mechanisms of intracluster energy exchange. Unfortunately, we failed to form a sufficient number of particles of a different molecular composition in a clustered flow using a high-voltage electron beam. The process turned out to be beyond the sensitivity of the mass spectrometric equipment.

In this paper, an alternative version of the process is considered: first, the formation of a low-temperature plasma in the flow, and then the formation of clusters of excited and ionized particles due to the creation of conditions of a sufficiently high density in the flow in the immediate vicinity of the nozzle for the formation of clusters.

2 Scheme of experiments

Experimental studies were carried out on the setup LEMPUS-2 of the Applied Physics Department by the Novosibirsk State University [5]. To detect ions formed in a supersonic flow by a well-focused high-voltage electron beam crossing the jet at a selected distance from the nozzle exit, a diagnostic system was developed and implemented at the facility with the transport of the formed ions to the quadrupole detector of the molecular-beam system by focusing with electrostatic lenses, which are used as a skimmer and collimator [3]. In the present work, this system is adapted for use in the regimes of gas or gas mixture ionization in the diffuser part of a supersonic nozzle. A specially made supersonic nozzle with an ionizer installed on it was used for this. The scheme of this nozzle is shown in Fig. 1.

The ionizer (1) and the ring magnet (2) with a dielectric (3) between them are fixed on an insulator (4) located on the metal base of the nozzle (5). Voltage is applied to the ionizer. As a result, an electric discharge occurs between the ionizer and the nozzle. The ring magnet focuses the discharge in the local area of the supersonic nozzle. The discharge current reaches $I_{ch} = 20 \div 30$ mA. The gas flowing through the nozzle is ionized by an electric discharge. Since the discharge action is

concentrated in the region of the nozzle, where the jet has the maximum density, the probability of excitation and ionization of the jet particles is much higher than in the previously used scheme with gas ionization by an electron beam. A molecular beam is formed from an ionized gas jet using a skimmer.

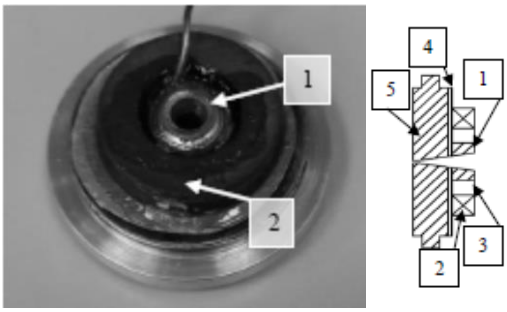

Fig. 1. Supersonic nozzle with ionizer D*=0.17 mm, Da=4.45 mm, L=14 mm: 1 – ionizer; 2 – ring magnet; 3 - dielectric; 4 - insulator; 5 - metal base.

A schematic diagram of the equipment used and the experiments is shown in a Fig. 2. In the expansion chamber (1), a prechamber with a nozzle (2) is installed on the coordinate movement device. The prechamber with nozzle (3) is brought out onto the axis of the molecular-beam system. The voltage supply to the nozzle is carried out through the input (4) from the source U_{ch} (5). The gas jet (6) flowing from the nozzle can intersect with the electron beam (7) generated by the electron source (8) in the electron gun section (9). The developed technique includes a system for extracting ions to the detector of a mass spectrometer. This system consists of a skimmer (10) and a collimator (11), electrically isolated from the rest of the installation and connected to separate voltage sources (12), (13) through electrical inputs (14) and (15), respectively. Passing through the post-skimmer section (16), collimator (11) and detector section (17), the ionized molecular beam (18) reaches the input diaphragm of the quadrupole mass spectrometer (19), which has its own ionizer disabled. The facility is pumped by the differential system of vacuum pumps (20). This system provides a pressure of about 10^{-1} Pa in the expansion chamber, 10^{-4} Pa in the post-skimmer section, 10^{-6} Pa in the detector section and 10^{-2} Pa in the electron gun section. The source of electrons (8) is a hollow cathode. An electron beam (7) with parameters U_{eb} = 10 kV, I_{eb} = 30 mA is collected by an electron collector (21).

Note that due to the flow of electric current through the nozzle, it will heat up, and the ring magnet used in the design will gradually lose its magnetic properties. Therefore, this nozzle was equipped with a thermal sensor and the experiments carried out in the future were limited in time in order to minimize damage to the nozzle during usage.

3 Results and discussion

3.1 Ion current in a molecular beam upon ionization of a gas jet by an electron beam and an electric discharge in a nozzle

To evaluate the efficiency of the new method of gas flow ionization, we compared the ion current in a molecular beam in two cases: when the gas flow is ionized by an electric discharge and by an electron beam. To do this, a Faraday cylinder was installed on the jet axis in the post-

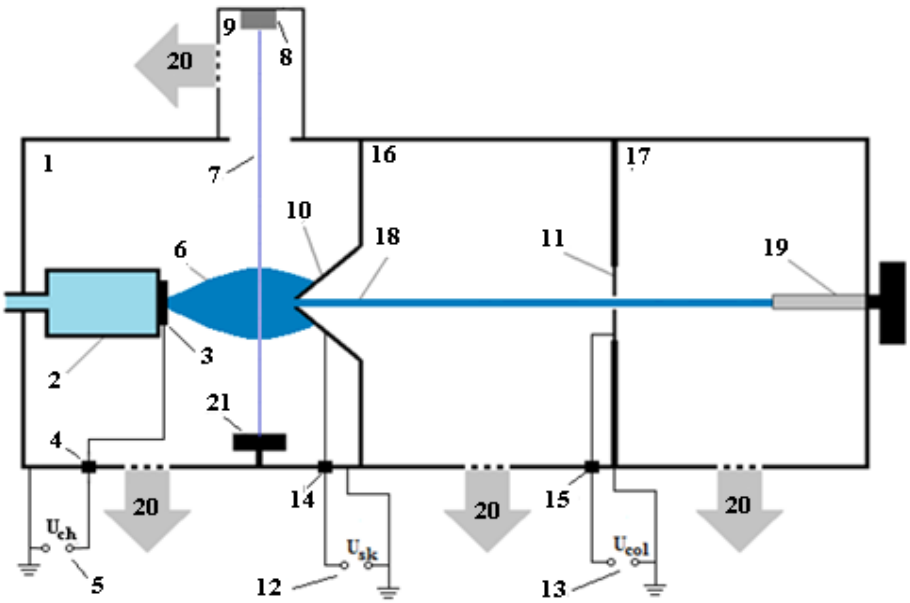

Fig. 2. Schematic diagram of diagnostics by molecular beam mass spectrometry with external gas ionization by a discharge in the nozzle at the facility LEMPUS-2: 1 – expansion chamber; 2 – prechamber; 3 - nozzle with an ionizer installed on it; 4, 14, 15 - electrical inputs; 5 - power supply system for the nozzle with an ionizer; 6 - gas jet; 7 – electron beam; 8 – source of electrons; 9 - section of the electron beam; 10 - skimmer (Ds=0.49 mm, angle 50x55°); 11 - collimator (Dcol=1.75 mm); 12 – power supply system for the skimmer; 13 – power supply system for the collimator; 16 - post-skimmer section; 17 - detector section; 18 - molecular beam; 19 – quadrupole detector of the mass spectrometer with the ionization unit disabled; 20 - vacuum pump; 21 - electron collector.

skimmer section and connected to the load through one of the electrical inputs of the installation.

The measurements were carried out at stagnation pressures $P_0 = 50 \div 300\ kPa$. Argon was used as a model gas. In the case of gas ionization by a discharge in the nozzle, an ion current I_i^{ch} from 5 to 45 nA, was recorded, while in the case of ionization by a high-voltage electron beam under similar gas-dynamic conditions, the ion current I_i^{eb} was from 0.1 to 2 nA, i.e. much less.

Thus, we can conclude that gas ionization by an electric discharge in a nozzle is more efficient than ionization of a gas jet by an electron beam.

3.2 Optimization of the ion extraction system for the case of ionization by a discharge in a nozzle

The formation of a molecular beam from a supersonic jet was carried out according to the standard scheme. Under these conditions, the delivery of ions to the mass spectrometer was performed by a skimmer and a collimator used as electrostatic lenses. Optimization of the potentials applied to the skimmer and collimator was performed earlier. However, since the configuration of electromagnetic fields is different during gas ionization by an electric discharge in the nozzle, it was necessary to optimize the extraction potentials for the new diagnostic technique in order to better focus ions on the entrance aperture of the mass spectrometer with its own ionization unit turned off. Calibrations were carried out on model gases, argon and nitrogen in the stagnation pressure range of 50 ÷ 300 kPa. It has been established that the optimal potentials on the skimmer and collimator are -50 and -300 V, respectively. Subsequently, all experiments were performed at these potentials.

3.3 Registration of clusters during gas ionization by an electric discharge

The use of quadrupole mass spectrometry of molecular beams under conditions of flow clustering faces a number of fundamental problems. First, the electron ionization of clusters leads to their destruction. In this case, small clusters decompose mainly into monomers and dimers, while large clusters mainly decompose into large fragments. Secondly, there is, as a rule, a significant limitation of the range of recorded masses. In the present cases, the quadrupole mass spectrometer provided a range from 1 to 1000 amu. At the same time, the average size of argon clusters in typical experiments can reach 40000 amu and more. Under such conditions, it is possible to register only a small amount of relatively small fragments in terms of composition, or the implementation of regimes with the formation of clusters of only small sizes and the construction of models that describe the true composition of the clast flow from the registered set of fragments.

Therefore, a series of pilot experiments was carried out to diagnose gas flows of argon and nitrogen by molecular beam mass spectrometry with ionization of the gas flow by an electric discharge in the nozzle. Argon was used as the main condensable carrier gas for further studies, while nitrogen was used to compare the results with a significantly lower ability to cluster formation under similar conditions. The stagnation pressure was varied in the range from 100 to 400 kPa.

The graph of the registered signals depending on the cluster size is shown in Fig. 3: (a) in argon and (b) in nitrogen.

In an argon jet (the average cluster size in all dimensions exceeds 100), according to Fig. 3(a), monomers and dimers are mainly registered when using a discharge in the nozzle. It should be emphasized that, in these measurements, signals of lower intensity are strongly noisy and therefore unreliable.

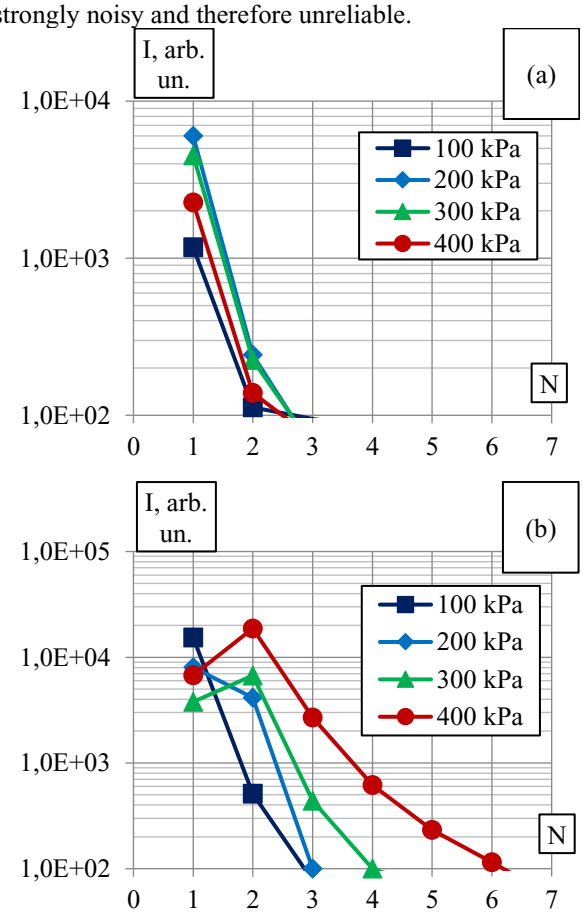

Fig. 3. Signal intensity depending on the cluster size of (a) argon and (b) nitrogen for stagnation pressures of 100, 200, 300, and 400 kPa. Nozzle-skimmer distance X = 60 mm.

In a nitrogen jet (the average cluster size does not exceed 20), as can be seen from Fig. 3(b), large clusters, up to pentamers, are also reliably recorded. Apparently, in a flow with argon, taking into account the technique used and the available sensitivity of the equipment, it is difficult to expect the observation of cluster fragments larger than a dimer. It should also be taken into account that, for technical reasons, the nozzle-skimmer distance cannot be reduced without the risk of losing the sharpness of the inlet spout due to the impact of charged particles. Therefore, the ions formed in the nozzle have the opportunity not only to participate in cluster formation, but also in collisional processes on the way from the nozzle to the skimmer.

3.4 Ionization in the nozzle of gas flows of mixtures 80%Ar+20%CH_4 and 80%He+20%CH_4

The results of the discharge through a nozzle with discharge ionization are considered in mixtures of methane (20% volume concentration) with two carrier gases, argon and helium. The mass spectra of the 80%Ar + 20%CH_4 gas mixture for three stagnation pressures of 50, 100, and 200 kPa are shown in Fig. 4. In this case, the intensity of the peaks decreases with increasing stagnation pressure. Since the average size of clusters should increase with increasing stagnation pressure, this result can be explained both by an increase in the fraction of clusters and by the efficiency of the discharge ionization process at different gas densities in the nozzle region.

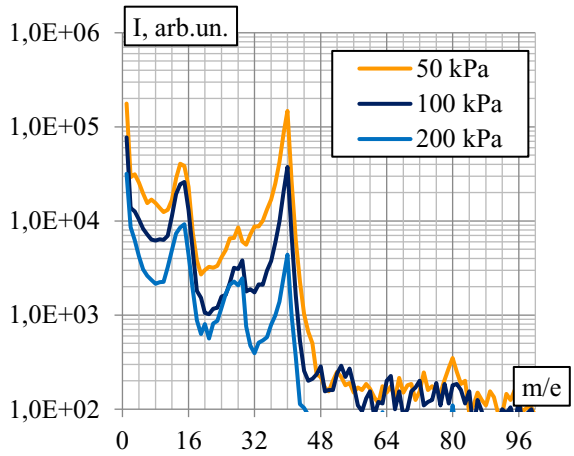

Fig. 4. Mass spectrum of the gas mixture 80%Ar + 20%CH_4. Distance nozzle - skimmer X =45 mm.

The signals on all the given mass spectra are clearly distinguished for the masses corresponding to the ions H^+, H_2^+, CH_x^+ (x=0-4) and Ar^+. Note that a weak peak of ion Ar_2^+ is observed only at the minimum stagnation pressure. Presence of ions H^+, H_2^+ in the flow is obviously caused by the destruction of methane during gas ionization by an electric discharge in the nozzle. At masses around m/e = 28 and less distinctly – 32 fragments of dimer ions are registered $(CH_2)_2^+$ and $(CH_4)_2^+$. Another version of the presence of peaks at masses m/e = 27-29 may be the synthesis of ethylene (C_2H_4) from methane clusters.

Mass spectra of a gaseous mixture of methane with noncondensable helium 80%He + 20%CH_4 are shown in a Fig. 5 for braking pressures 100 and 200 kPa.

In contrast to the mixture with argon, the intensity of characteristic peaks increased with increasing stagnation pressure, and at a stagnation pressure of 200 kPa, peaks related to small methane clusters up to and including pentamer were reliably recorded. Apparently, unlike argon, helium does not prevent the condensation of methane in the mixture flow. In this case, as it should be for a small cluster size, an increase in the stagnation pressure stimulates the process of cluster formation. One could also consider the possibility of identifying the peaks of the series $(CH_4)_{n-1}CH_{x+1}^+$ (n = 1 ÷ 5, x = 0 ÷ 5) as a consequence of the reactions of the synthesis of new products, however, at this level of sensitivity of diagnostic equipment, it is premature to discuss such versions.

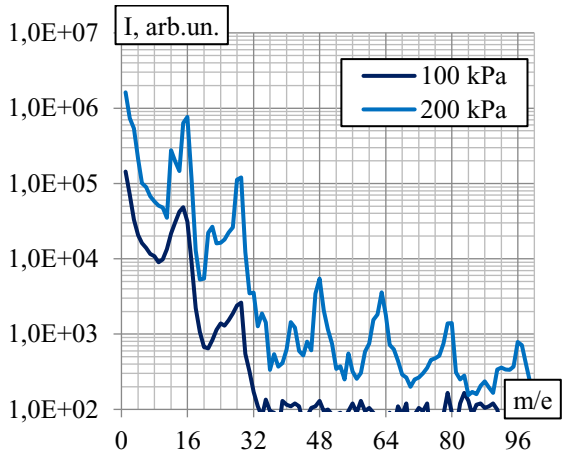

Fig. 5. Mass spectrum of the mixture 80%He + 20%CH_4. Distance nozzle - skimmer X =45 mm.

4 Conclusions

The diagnostics of cluster ions by the method of molecular-beam mass spectrometry during gas ionization by an electric discharge in a nozzle and further, downstream, by the formation of clusters, has been implemented and debugged. A nozzle with a system for generating an electric discharge in the diffuser part of the nozzle was designed and implemented. The adaptation of the LEMPUS-2 gas-dynamic unit for recording gas flows using the developed diagnostics has been performed.

When using argon as a model gas, it was found that gas ionization by an electric discharge in a nozzle is more efficient and allows recording a larger number of ions than when a gas jet is ionized by an electron beam.

A series of trial experiments on the diagnostics of gas flows of argon and nitrogen during the ionization of a gas flow by an electric discharge in a nozzle has been carried out. Cluster ions up to pentamers were detected during the outflow of molecular nitrogen, which condenses weakly under experimental conditions.

A mass-spectrometric study of the products of ionization and cluster formation during the outflow of gas mixtures of methane (20% by volume concentration) with two carrier gases, well condensable argon and practically non-condensable helium, was carried out. As a result, it was determined that when the mixture of methane with argon flows out, ions of methane monomers and dimers, as well as their fragments, are recorded. Cluster ions of methane up to and including pentamers have been registered during the outflow of a mixture of methane with helium at a stagnation pressure of 200 kPa. A version of the explanation of the discovered dependencies is presented.

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