Plasma chemical reactions initiation in supersonic jets by a high-voltage electron beam

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Abstract. The results of the study of processes occurring in supersonic flows of gas mixtures under the influence of high voltage electron beam are presented. The research was performed on the gas-dynamic complex of experimental installations located in the Department of Applied Physics of Novosibirsk State University. Spectral methods and molecular beam mass spectrometry were used to diagnose the processes. A significant difference in the clustered argon mass spectra was found in comparison of spectrum recorded during ionization by a quadrupole mass spectrometer own ionizer and spectrum obtained with the transport of ions formed by an electron beam in the jet through a skimmer to the mass spectrometer detector (without using an ionizer of spectrometer). The second variant of gas flow ionization presents the possibility of registering the mass spectrum of a hydrocarbon series with features indicating the occurrence of heavier hydrocarbons in the jet. The mechanism of intracluster energy exchange with the transfer of excitation initiated by electrons with subsequent intense radiation at certain wavelengths of a neutral argon atom was detected and identified.

1. Introduction

A supersonic jet of gas or gas mixture flowing from a sonic or supersonic nozzles into a rarefied medium is an extremely interesting object for researchers for a number of reasons. First, the forming jet is usually protected from the external environment by side and closing shock waves, which allows to study the processes occurring in the flow without external influences. Secondly, due to the sharp expansion of the gas behind the nozzle, the vibrational, rotational and even translational degrees of freedom of the molecules can be frozen, which allows to study the relaxation processes and energy exchange between individual degrees of freedom of the molecules. Third, it is easy to create conditions for cluster formation in the jet, and it is possible to vary the achieved average size of clusters from dimers to thousands of particles. Finally, the impact on the jet particles by electrical discharge allows to initiate collisions between neutral, excited and ionized particles with the formation of new structures.

Our experience has shown that molecular beam mass spectrometry of supersonic condensing flows in the traditional form, with skimming of the neutral gas flow and ionization of the molecular beam in the mass spectrometer detector (despite its high informational content) has a number of disadvantages due to the gas-dynamic aspects of the molecular beam formation, which includes monomers and clusters of different sizes [1-2]. In addition, such a scheme of experiments excludes the possibility of studying the processes occurring in the jet by the presence of ionized particles.

We debugged the scheme of supersonic jet ionization at different stages of expansion using a well-focused relatively high energy (about 10 keV) electron beam with followed transport of ionized
particles through a skimmer and collimating diaphragm to the mass spectrometer detector when its own ionizer is turned off [3]. Comparison of data obtained with and without supersonic jet ionization allows to study the role of ionized particles in the supersonic expansion and collision energy exchange process.

Of course, the authors understand that ions undergo collisions with neutral particles both before skimming (since the jet density is quite high) and in the molecular beam (due to the speeds difference). In ionization, some of the clusters can decompose into fragments; as a result of collisions of neutral clusters with ionized particles and ionized clusters with neutral particles, recharge and exchange of energy can occur. Other processes, that require careful and detailed consideration and accounting, may also be. However, using a combination of a high-voltage electron beam in a jet with mass spectrometry allows to significantly expand the range of processes under study. In this paper, we present several examples of studies of processes occurring in supersonic gas mixtures flows excited by a high-voltage electron beam.

2. Experimental equipment
The research was performed on the gas-dynamic complex of experimental installations LEMPUS-1 [4], LEMPUS-2 [5] and PKHUS [6] of Novosibirsk State University. Spectral methods and molecular beam mass spectrometry were used to diagnose the processes. The schematic diagram of the main experiments is shown in figure 1.

![Figure 1. Schematic diagram of measurements](image)

Gas source (pre-chamber with a sonic or supersonic nozzle) (1) is located on a coordinate device (2) provided movement of the nozzle relative to the stationary electron beam (3) and skimmer (4) of the molecular beam system. The X-axis of the supersonic jet (5) coincides with the molecular beam axis. The electron beam used in experiments in conjunction with molecular beam measurements is perpendicular to the X-axis. As a rule, the electron beam Z-axis strictly intersects the jet axis. The optical scheme collects radiation excited by an electron beam in a gas jet through a quartz window (6) by a lens (7) into spectrometer (8) placed outside the vacuum chamber on its own coordinate device (9). The Y-axis of the optical device is orthogonal to the other two axes. This system is easily adjusted and provides a high locality of optical measurements. The movement of the gas source and jet by using the coordinate mechanism allows exciting the radiation at any point in the flow (except for distances close to the nozzle due to heating by scattered electrons and electromagnetic distortion of the electron beam by grounded pre-chamber).

The skimmer of molecular beam device for mass spectrometric analysis cannot be located at the same point where the electron beam intersects with the gas flow axis. The optimal distance has been selected to ensure that the skimmer is not damaged by the electron beam. Thus, the area of gas-plasma flow selected to the molecular beam system is located at a certain distance from the activation area by electrons. The molecular beam device is made as a traditional two-section scheme with differential pumping of the post-skimmer chamber (10) and (separated by collimating diaphragm (11)) detecting chamber (12) with the quadrupole mass spectrometer (13). Electric potentials could be applied to the
skimmer, collimator, and input aperture of the mass spectrometer detector, which provides optimal conditions for the passage of charged jet particles to the mass-spectrometer [7].

3. Results
This part will demonstrate only some experimental results, which mostly effective characterize the main focus of research.

3.1. Cluster fragments registration in a supersonic jet
Most mass spectrometry methods are based on ionization of neutral particles by electrons. The electron energies used for this purpose usually range from a few tens to several hundred eV. When using an electron beam to diagnose a supersonic jet, the electron energy can reach several tens of keV. Since gas clusters are bound by van der Waals forces with connection energy less than 1 eV, ionization of clusters is accompanied by their destruction. As is known, small clusters break up mainly into monomers and dimers, while large clusters - into large fragments [8-12]. The process in this case is probabilistic and depends on the size, structure and composition of clusters, as well as on the electrons energy. Therefore, measuring the size distribution of clusters and obtaining large clusters during supersonic jet expanding into a vacuum is a very difficult task.

Figure 2 shows the comparison of mass spectra obtained in a supersonic jet of molecular nitrogen, as recorded with mass spectrometer ionization unit with an electron energy of 70 eV ("inner ionization") and by transport into the mass spectrometer ions formed in the jet by high-voltage electron beam with energy 10 keV ("outer ionization"). In both cases, the gas dynamic parameters were the same: stagnation pressure ($P_0 = 140$ kPa), stagnation temperature ($T_0 = 298$ K), the nozzle configuration and nozzle – skimmer distance. For ease of comparison, only mass peaks maximum values are given. Blue indicates data for internal ionization, red – for external ionization. The graph shows mass spectra normalized by the sum of the peak amplitudes of the registered masses.

![Figure 2. Comparison of mass spectra recorded using molecular beam mass spectrometry in a supersonic nitrogen jet with two ionization variants.](image)

Attention is closed to the fact that in standard mass spectrometry ("inner ionization") the intensity of the $N_2^+$ monomer ion and its dissociative part $N^+$ with a sharp drop in the amplitudes of cluster peaks is dominated. For example, the ion peak of the nitrogen ($N_2)_2^+$ dimer is almost two orders of magnitude smaller than the monomer peak. At the same time, by external ionization, the dimer ion amplitude is comparable to that of a monomer, and the nitrogen tetra - and pentamer ions, i.e. ($N_2)_4^+$ and ($N_2)_5^+$, are almost identical in amplitude, only an order of magnitude smaller than the monomer. In this case, approximately an order of magnitude smaller amplitudes are registered at the peaks ($N_2)_S^+$ ($S = 2, 3, ...$ is the number of molecules in the cluster). This may be due to changes in the process of cluster destruction at high electron energies (this was noted by the authors [10]), as well as to conditions for collisions of neutral and charged particles after ionization. A detailed comparison of the results and assumptions about the reasons for the differences can be discussed. In any case the proposed method of ionization in the jet allows obtaining a wider composition of clusters.
3.2. The conversion of methane in clustered flow

Attempts to use flows of weakly ionized plasma (various types of electric discharges, plasma torches, accelerators were used) to initiate reactions that lead to the processing of volatile hydrocarbons (methane, ethane, etc.) into "heavy", i.e. liquid under normal conditions, were made repeatedly [13-22]. These attempts were stimulated, first of all, by the obvious advantages of gas – plasma flows – huge interaction cross sections, as a result – the ability to accelerate the conversion of hydrocarbons. This, in turn, could be provided the compactness of devices with high performance. However, to date, all these advantages have been successfully implemented only at the first stage of the process: the radicals necessary for starting the synthesis are formed successfully, but it has not yet been possible to organize an effective process to heavy hydrocarbons synthesis.

The authors have studied the possibilities of a different approach: the formation of clusters in a supersonic flow containing light hydrocarbon molecules and carrier gas atoms in certain proportions (argon, helium), and the subsequent initiation of the clustered flow by an electron impact. Some molecular beam mass spectrometry results of the ion component in such flows are shown below.

Figure 3 shows the spectrum in the mass range of monomers and dimers in a jet of a mixture of CH$_4$ (20%) + He (80%). It can be seen that in addition to the peaks corresponding to the methane radicals CH$_n^+$, where $n = 4, 3, 2, 1$, there are intense peaks m/e = 29, 30, 40, 41, which are typical for mass spectrometry with electron ionization of higher hydrocarbons [23].

It is found that in a mixture of methane with a monatomic gas, by varying the composition of the initial mixture and the stagnation parameters, it is possible to effectively control the size, composition and structure of clusters. As shown in figure 4, with increasing stagnation pressure, the initial ratio of methane peak intensities sum compared to the same for the carrier gas (argon) changes from predefined by a given mixture composition, to a significant methane excess over argon in conditions of intense condensation. This result confirms the predominance of large methane and mixed clusters on the molecular beam axis.

Another notable feature of the methane mass spectra obtained by expanding the methane - monatomic gas mixture is the regular formation of cluster protonated particles. Separate parts of the mass spectrum registered by a quadrupole mass spectrometer in methane – helium mixture (20 : 80) are shown in figures 5 – 7. The intensity of the peaks (CH$_4$)$_m$CH$_5^+$ (m = 1, 2,...) increases with the growth of m/e in comparison with the particles (CH$_4$)$_m^+$. With further m/e growth, at m > 10, clusters of (CH$_2$)$_m$CH$_{3}$ and even (CH$_3$)$_m$CH$_{3}$ are detected, the comparative intensity of peaks of which also increases. Another fact is the systematic formation of cluster peaks of the type (CH$_4$)$_m$CH$_+$.

In results, the initiation of a clustered flow using an electron beam can cause the following processes: the flow heating and, consequently, a decrease in the proportion of condensate, both by reducing the clusters concentration and by decrease their average size; electron-stimulated condensation, when ionized particles become the clusters nuclei, resulting in an increase the number of clusters and the condensate proportion; electron cross-linking of molecules in a cluster, when, due to
interaction with an electron beam, hydrogen atoms are knocked out of the cluster, and the remaining radicals are bound into stable molecules of heavier hydrocarbons

**Figure 5.** 20%CH\(_4\)+80%He mixture mass spectrum with S clusters size from 4 to 12.

**Figure 6.** 20%CH\(_4\)+80%He mixture mass spectrum with S clusters size from 16 to 31.

**Figure 7.** 20%CH\(_4\)+80%He mixture mass spectrum with S clusters size from 45 to 62.

### 3.3. The high intensity radiation in the argon flow with methane and silane admixtures

Anomalous argon radiation in the discharge has been studied by many authors (see, for example, the review [24]). In [25], an abnormal argon radiation increase in the supersonic flow of argon – silane mixture was detected during activation by fast electrons. Technical limitations did not allow the authors of this work to study in detail detected effect conditions, although they suggested the role of condensation process. In figure 8 we present some results of studying on our equipment this glow effect. The measurements were performed in condensing supersonic argon flows with small admixtures of methane and silane under electron-beam activation with an electron energy of 10 keV. The radiation spectra excited by an electron beam in jets of pure argon and mixtures of Ar with 5% of He, CH\(_4\) and SiH\(_4\) were obtained in the range of \(P_0 = 10 \div 700\) kPa at \(T_0 = 298\) K.

It was found that the intensity of lines of one-shot ionized argon (ArII) increases linearly with increasing stagnation pressure over the entire studied range. Only at high values of \(P_0\), and, consequently, local jet density, the growth of radiation intensity is slowed down due to collision quenching [26-27]. An intensity of ArII spectral line radiation with a wavelength of \(\lambda = 460.96\) nm (the blue part of the spectrum) was chosen as a reference value, with which the intensities of all other spectral lines were compared.

In the neutral argon (ArI) spectrum a nonlinear effect was registered only on several lines in the range 540 – 580 nm (the green part of the spectrum). One of the most intense was the radiation line of...
an excited argon atom with a wavelength of $\lambda = 549.59$ nm. This line will be used in further measurements. Figure 8 shows that the argon atom radiation intensity depends on the gas mixture composition. In a pure argon jet as well as in a mixture with helium, there are no features in the registered dependence on $P_0$. On the contrary, in mixture flows of argon with methane or silane, the radiation intensity of the argon atom sharply increases after a small section of linear growth, and with a further increase in pressure returns to the initial linear approximation (black continuous lines). The stagnation pressures range of observed deviation is depends on the mixture composition.

![Figure 8. The dependence of the spectral lines intensities for neutral argon, ArI (light icons), and ionized argon, ArII (darker icons), on the stagnation pressure.](image)

The recorded radiation intensity normalization to a linear approximation of the initial parts of these dependencies allowed to determine the boundaries of the effect. Figure 8 clearly shows the boundaries of the anomalous increase in the radiation intensity of atomic argon. In addition, it is possible to estimate the contribution to the argon atom excitation from a nonlinear effect that causes an abnormal increase in intensity, in comparison with the radiation excitation by a direct electronic impact according to the linear law. A multiple increase in the radiation intensity in comparison with the linear approximation indicates that a highly efficient collision excitation channel is involved in the process, which is associated with an abnormally large energy exchange cross-section. Mass spectrometry and subsequent analysis showed that the range of the observed effect is due to the presence of mixed clusters of a certain size in the supersonic jet. The inverse pumping mechanisms of neutral argon levels with the participation of clusters are discussed in this report.

### 4. Conclusion

The high-voltage electron beam use in gas and gas mixture supersonic jets to initiate the processes of atom or molecule excitation and ionization, including those united in clusters, in combination with molecular beam mass spectrometry of the resulting compounds composition provides new opportunities for studying plasma chemical processes in a rarefied medium.

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