Features of the methane clusters formation in supersonic jets of methane and its mixtures with monatomic gases

A E Zarvin, V E Khudozhitkov and V V Kalyada
Department of applied physics, Novosibirsk State University, 630090, Novosibirsk, Russia
E-mail: zarvin@phys.nsu.ru

Abstract. This work demonstrates the methane clusters formation in supersonic free jets of methane mixtures with helium and argon. The dependence of the clusterization process properties on the carrier gas, the volume fraction of methane in the mixture at the selected gas jet parameters is shown. Impact of the methane dissociative ionization, and methane clusters fragmentation in the detector of the mass spectrometer on the process of condensation was demonstrated. The presence of protonated cluster ions of methane and the increase in their proportion with growing size of clusters was established. The formation of cluster ions with an attached methyl, methylene or methylidene was discovered.

Methane is widely used for the films deposition, because the plasma-chemical decomposition of methane allows the growth of diamond-like carbon, amorphous carbon films, polycrystalline carbon films, and carbon nanotubes. The use of methane clusters as a raw material for application to the surface may provide the creation of new nanomaterials with unique properties. The conventional method of obtaining atomic and molecular clusters is an adiabatic expansion of a gas with the desired composition from the stagnation chamber at known pressure and temperature using sonic or supersonic nozzle with a given geometry and at a sufficient rarefaction [1]. There have been reported several attempts to obtain large clusters of methane in streams of pure methane (see e.g. [2–3]). However, in contrast to the monosilane [4], at a supersonic expansion of pure methane the registration of large clusters can be achieved only at high stagnation pressures (tens of atmospheres) and/or low temperatures [5]. At the same time, clusters of methane and mixed argon-methane complexes are registered in a mixture with a carrier gas (argon) under moderate stagnation parameters as well [6]. Among the reasons of such clusterization peculiarities in the methane jets with carrier gas is primarily the entrainment of excess energy by argon during the formation of the oligomeric molecular gas cluster (triple collisions) [4–5]. The molecular hydrogen was also tested as such a “cold” reservoir [2].

The active use of argon as a carrier gas leaves a number of unresolved problems. Firstly, argon is easily condensed. Its condensation can also be the reason of oligomers nucleation, which can initiate the formation of binary supramolecular structures. Secondly, argon is a heavy gas compared to methane. This leads to the displacement of methane to the periphery of the supersonic jet. Therefore, it seems preferable to use lighter gas as the carrier gas, which condenses at much lower temperatures than methane. It is obvious that hydrogen or helium should be used as carrier gas. In our opinion, helium is more preferable, firstly, because with the expansion of a monatomic gas the temperature drops faster, and, secondly, it is possible to directly compare the processes taking place in a supersonic...
jet of the various mixture. Investigations of supersonic expansion of binary mixtures with the possibility of methane condensation with a carrier gas are of the interest both as a prospect for obtaining pure one-component large-scale methane clusters and as an object of studying the formation processes of binary clusters.

In this paper, the analysis of the formed clusters was carried out using the method of molecular beam mass spectrometry at the gas-dynamic LEMPUS-2 complex of Novosibirsk State University [7]. A quadrupole mass spectrometer Hiden Analytical EPIC 1000 with a dynamic range of 2–1000 a.m.u. was used. Mass spectra were recorded at the electron energy 70 eV in the ionizer of a mass spectrometer. A supersonic jet was formed as a result of the expansion through a supersonic nozzle with a critical section diameter $d_*$ = 0.17 mm, a diffuser length $L_d$ = 8.2 mm and an output diameter $D_a$ = 2.2 mm. The following parameters of the stagnation in the nozzle pre-chamber were maintained: pressure $P_0$ = 0.3 MPa, temperature $T_0$ = 298 K. We have chosen the entrance diameter of the molecular beam system skimmer $d_s$ = 0.44 mm. As a result, a sufficiently wide range of nozzle-skimmer distances was provided, in which both external and internal skimmer interaction could be neglected [8]. The pumping system provided a vacuum in the chamber of the mass spectrometric detector at the level no worse than 0.02 mPa. The sensitivity range of the mass spectrometer was about 7 orders of magnitude, from $10^0$ to $10^7$, but the amplitudes at a level less than $2 \cdot 10^1$, as a rule, were neglected because of the high noise of the useful signal.

In our work, experimental studies of the supersonic jets of helium-methane mixtures were conducted with the following component ratios (in volume percents): 90 – 10, 80 – 20, 60 – 40, 40 – 60, 20 – 80, 10 – 90, and also in pure methane and in an argon-methane mixture with a component ratio of 80 to 20.

It is established that clusters of methane in a mixture with helium are formed much more efficiently than in a mixture with argon. Earlier we found out [6] that oligomers $\text{Ar}_n^+$, $(\text{CH}_4)_m^+$, and also $(\text{CH}_4)n\text{Ar}_k^+$ (where $k$, $l$, $m$, $n$ – are integers) are registered at a volumetric methane content in argon of 10, 5 and 2.5 percents in the supersonic flow of such mixtures. The presence of clusters of both components in the mixture, as well as mixed clusters, confirmed the existence of parallel nucleation processes in argon and methane.

Figure 1 shows the mass spectra of helium-methane and argon-methane mixtures at the same volume concentration of methane (20 %). As noted above, the data are compared under the same stagnation conditions, the nozzle geometry and the molecular beam system at a fixed distance from nozzle to skimmer (40 mm).

![Figure 1. Histogram of mass spectra with two carrier gases, Ar (red lines) and He (green lines) within the range up to m/e = 100.](image-url)
The amplitude of the mass peaks is normalized to the sum of the peaks of all masses. Naturally, this normalization cannot give a completely objective comparison of different mixtures, however it provides an opportunity to draw certain conclusions.

In both mixtures, there is a traditional distribution of the amplitudes of \( \text{CH}_x^+ \), where \( x = 0, 1, 2, 3, 4 \). Also, in both mixtures the amplitudes of methane monomers predominate over the carrier gas amplitudes. This indicates the intensive formation of methane oligomers with effective fragmentation of such clusters, mainly up to monomers. The intense peaks \( m/e = 18 \) and \( 17 \) are related to the water vapor background presence, not eliminated by the pumping system of the molecular beam detector chamber. The presence of an intense hydrogen peak, as well as a set of \( \text{C}_n\text{H}_m^+ \), peaks characteristic for mass spectra of the hydrocarbon cycle (\( m/e = 27, 29, 39, 41, 43, 55, 57, \) etc.) can be explained by the dissociative ionization of methane and the destruction of methane clusters during the electron impact and the existence of fast ion-cluster reactions during the detection period of registered ions in the detector of the mass spectrometer, which is \( 2 \cdot 10^{-4} – 2 \cdot 10^{-5} \) sec. It should be noted that such peaks in the range up to \( m/e \sim 100 \) have larger amplitude than the cluster peaks, except for the dimer (in mixture with helium). With further growth of the mass number, the intensity of the hydrocarbon cycle peaks drops sharply, while the cluster peaks are observed throughout the recorded mass range.

In the given range, the differences between the two spectra are insignificant except for the masses, which should be attributed to He and Ar. One can only note the presence of more intense peaks of the hydrocarbon series radical fragments in a mixture of methane and helium. In contrast to the data [8] obtained in a mixture with argon at a lower concentration of methane, in our measurements no appreciable peaks related to argon oligomers or mixed argon-methane clusters were recorded.

The mass-spectra of larger clusters, \( N > 6 \) (where \( N \) is the cluster size), depending on the mass number \( m/e \), are shown in figure 2. For convenience, the ordinate is given on a linear scale. The maximum values of the amplitudes of neighboring peaks are connected by straight lines.

As can be seen from the graph, the methane clusters are much larger in amplitude in the mixture with helium (green lines) than with argon (red lines). This confirms the assumptions about the efficiency of heat removal by light gas, as well as the possible parallel process of argon condensation in mixtures with methane that retards methane cluster formation.

![Figure 2](image.png)

**Figure 2.** Graph of changes in the amplitudes of mass peaks \( I_n \) in mixtures of methane with argon (red lines) and helium (green lines) with normalization to the sum of the amplitudes of all peaks, depending on the mass number.
Measurements with other compositions of mixtures showed that with increasing percentage of methane in the mixture, the fraction of large clusters decreases, i.e. the process of cluster formation is weakens. In the mixtures where the volume concentration of methane exceeds 40 %, methane clusters have not been detected with the exception of a small number of dimers and trimers.

The mass spectrum of a mixture of 20 % CH₄ + 80 % He with the same gas dynamic parameters in the cluster size range from \( N = 6 \) (\( m/e = 96 \)) to \( N = 34 \) (\( m/e = 544 \)) can be considered in more detail in figure 3. The mass numbers \( m/e \) are plotted along the abscissa axis, and the amplitude of the ion peaks in the logarithmic scale is plotted along the ordinate. For convenience, the mass spectrum is divided into two ranges, \( 6 \leq N \leq 20 \) and \( 20 \leq N \leq 34 \), listed consecutively, one under the other. Noteworthy, that with a further increase in the mass number, cluster peaks are also present, but in the above mentioned mode of gas dynamic parameters, the signal level at \( N > 40 \) is insufficient for the reliability of the results.

![Mass spectrum of the gas mixture 20 % CH₄ + 80 % He. The nozzle-skimmer distance – X = 40 mm, the stagnation pressure – \( P_0 = 0.3 \) MPa, the background pressure in the main chamber – \( P_b = 4.4 \) Pa, in the post-skimmer chamber – \( P_{ps} = 1 \cdot 10^{-3} \) Pa, in the detector chamber – \( P_d = 4 \cdot 10^{-5} \) Pa.](image)

**Figure 3.** Mass spectrum of the gas mixture 20 % CH₄ + 80 % He. The nozzle-skimmer distance – \( X = 40 \) mm, the stagnation pressure – \( P_0 = 0.3 \) MPa, the background pressure in the main chamber – \( P_b = 4.4 \) Pa, in the post-skimmer chamber – \( P_{ps} = 1 \cdot 10^{-3} \) Pa, in the detector chamber – \( P_d = 4 \cdot 10^{-5} \) Pa.

It can be stated that in a mixture with a small content of methane in helium, methane clusters reach a size of at least \( N > 50 \). Local maximums of amplitudes in the cluster peaks are detected, with \( m/e = 96, 224, 368, 576, 704 \), which corresponds to the size of the clusters \( N = 6, 14, 23, 36, 44 \). These maxima can be identified with the “magic” numbers [13] of cluster methane ions.

In addition to cluster ions of the \((\text{CH}_4)_n^+\) type, the protonated cluster ions of the \((\text{CH}_4)_n^+\text{H}^+\) type are observed. This feature was also found in a mixture of methane and argon [6]. Many studies have been devoted to the formation of protonated molecules. In the literature on mass spectrometry, the results of
protonation are described for some clusters [9–12]. However, the formation of protonated methane clusters requires a separate study. In this paper, we note that when the cluster size grows, the amplitudes of the protonated particles increase. Starting with cluster ions of size $n > 25$, the amplitude of such peaks becomes predominant. At the same time, noticeable amplitudes of twice protonated cluster ions are detected, the amplitude of which increases with the further growth of cluster size. The occurrence of protonated clusters indicates a possible presence of a substantially larger sized clusters in the investigated mixture flow that is inaccessible for the used mass spectrometric system.

It should be noted that in addition to the cluster peaks of the protonated series, we found in the spectrum of the mixture a cluster sequence of the type $(\text{CH}_4)^{n-1} \cdot (\text{CH}_m)^+\text{, where } m = 1, 2, 3$. Clusters with $m = 1$ and 3 have the highest intensity. The presence of clusters of this type confirms the process of ion-cluster reactions in the detector of the mass spectrometer and determines the lower bound of the rate of such reactions.

Acknowledgment
The work was performed using the equipment of the center for collective use "Applied physics" of NSU with the financial support of grants of the Ministry of Education and Science of the Russian Federation 3.5918.2017/ITR and 3.5920.2017/ITR.

References
[1] Haberland H 1994 Springer Series in Chemical Physics 52
[2] Yang S, Philippe L and Chatelet M 2007 International Journal of Mass Spectrometry 263 190–4
[3] Zarvin A E, Korobeishchikov N G, Khodakov M D and Kalyada V V 2012 Advances in Materials Physics and Chemistry 2 146–9
[4] Korobeishchikov N G, Zarvin A E, Madirbaev V Gh and Sharafutdinov R G 2005 Plasma Chemistry and Plasma Processing 25 319–49
[5] Abu-samha M, Ryding M J, Uggerud E, Sæthre L J and Børve K J 2017 The Journal of Chemical Physics 147 014301
[6] Zarvin A E, Kalyada V V, Korobeishchikov N G and Khodakov M D 2014 The Monthly Scientific and Production Journal «Nano Ingineering» 1 3–6
[7] Zarvin A E, Kalyada V V, Madirbaev V Gh, Korobeishchikov N G, Khodakov M D, Yaskin A S, Khudozhitkov V E and Gimelshein S F 2017 IEEE Transactions on Plasma Science 45 819–27
[8] Zarvin A E and Sharafutdinov R G 1979 Journal of Applied Mechanics and Technical Physics 20 744–9
[9] Smirnov B M 2003 Physics – Uspekhi 46 589–628
[10] Makarov G N Physics – Uspekhi 51 319–53
[11] Wyslouzil B E and Wölk J 2016 J. Chem. Phys. 145 211702
[12] Khodorkovskii M A, Artamonova T O, Murashov S V, Michael D, Rakcheeva L P, Belyaeva A A, Timofeev N A, Mel’nikov A S, Shakhmin A L and Dement’ev I A 2009 Tech. Phys. 54 1–6
[13] Eletskii A V and Smirnov B M 1989 Sov. Phys. Usp. 32 763–82