The role of carrier gas in cluster formation in methane supersonic jets

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Abstract. The influence of a monatomic carrier gas on cluster formation in supersonic methane jets is studied. The formation of methane clusters in a mixture with condensed argon and non-condensable helium with the same gas-dynamic parameters is then compared. It is shown that the methane clusters’ formation intensity is extremely low both within a jet of pure methane, and in a mixture with carrier argon. The methane condensation process dependence on the properties of a carrier gas and the methane volume fraction in the mixture at the selected gas dynamic parameters of the flow is demonstrated. The effect of dissociative methane ionization and the fragmentation of methane clusters in the mass spectrometer detector on the recorded mass spectrum is established. The cluster methane ions protonation and the increase in their fraction with increasing clusters are recorded. Finally, magic numbers for methane clusters are found.

1. Introduction

Methane and other hydrocarbon supersonic jets are widely used in the formation of thin carbon films, carbon nanotubes and fullerene-like structures [1-3]. Clusters formed in such jets allow for the reliable obtaining of coatings with other, possibly unique characteristics. However, numerous studies have shown that, despite their sufficient vaporization temperature which is quite comparable, for example, with argon, monosilane or nitrogen, the formation of clusters of a larger size than oligomeric within pure methane supersonic jets can only be induced within the gas source at pressures of more than several tens of atmospheres and/or temperatures close to cryogenic [3-6]. At the same time, methane clusters can be detected in argon flows with the addition of a small methane admixture [7]. The same result was obtained for jet mixtures of methane and hydrogen [6]. Since argon mixed with methane also can condense, argon-methane mixtures contain, in addition to pure argon and methane clusters, mixed clusters [7].

In our work, we demonstrated the possibility of obtaining large methane clusters in a supersonic jet. Based on the analyzed literature and our own experimental data we concluded that helium should be used as the carrier gas.

2. Equipment and methods

The work was performed on a LEMPUS-2 complex of low density gas-dynamic stands of the Applied Physics Department of the Physics Department of Novosibirsk State University [8]. The traditional molecular-beam diagnostics method was applied to register clusters. The supersonic jet of gas or gas
mixture was expanded through a supersonic nozzle into the rarefied space. With the help of a cone-shaped hollow diaphragm - skimmer, a molecular beam was formed and then introduced into the detector chamber through a subsequent collimating diaphragm. A Hiden Analytical EPIC1000 quadrupole mass spectrometer was used as a detector. All vacuum chambers of the device are provided with differentiated systems of high vacuum pumping, consisting of several turbomolecular and helium cryogenic pumps. The supersonic nozzle used in this work has the following parameters: the critical section diameter is \( d^* = 0.17 \) mm; the diffuser outlet diameter is \( D_a = 2.2 \) mm; the diffuser length is \( L_a = 8.2 \) mm. The diameter of the skimmer throat is \( d_s = 0.46 \) mm, the collimating diaphragm is \( d_c = 3 \) mm. The nozzle – skimmer distance \( L_{ns} \) was selected to minimize the influence of the skimmer’s interaction with the sample being taken into the molecular beam, and it was 40 mm in most of the experiments. The stagnation pressure \( P_0 \) in the above mentioned experiments was 300 to 400 kPa, the stagnation temperature \( T_0 = 298 \pm 1 \) K. High purity gases: argon - 99.999, helium - 99.99, methane - 99.99 were used.

We measured the mass composition of the clustered supersonic jets for gases and mixtures: 100% CH\(_4\), 80 to 10% CH\(_4\) in the He mixture, and 20% CH\(_4\) + 80% Ar. The mixtures were prepared in advance and fed into the nozzle pre-chamber in the finished form.

3. Results and discussion

Figure 1 shows the mass spectrum recorded in the pure methane jet. The amplitude of ion mass peaks, normalized to the sum of all peaks amplitudes, is plotted along the ordinate. The value of the mass number \( m/e \) is plotted along the abscissa. The main lines of the grid are plotted on the abscissa scale with an interval of 16 amu for the convenience of analysis. Accordingly, the peak \( m/e = 16 \), corresponding to the ion CH\(_4^+\), is to the left of the grid line corresponding to the value 17, and \( m/e = 17 \) - just to the right of it. The amplitude of the peaks decreases sharply with increasing \( m/e \). Purity of the source gas - methane provides a total amount of impurities in the initial gas flow within the range of 0.01%. Therefore, we limited the study to values exceeding 0.001%, despite the fact that the sensitivity limits of the mass spectrometer provide a measurement up to 8 orders of magnitude.

The spectrum contains significant water vapor peaks (\( m/e = 18 \) and 17) since water vapor is the most difficult to remove background residual component. This fact indicates that the background particles fall into the molecular beam from the nozzle chamber, since the background of the detector section is negligible. The peaks of ions with masses \( m/e = 28 \) (~3%), \( m/e = 32 \) (~0.2%) and \( m/e = 44 \) (~1%) are observed in a much lesser amount. The large fraction of hydrogen (about 10%), the presence of carbon dioxide and the small portions of typical mass spectrometric peaks of hydrocarbon radicals (\( m/e = 27 \) and 29, 39 and 41, 55 and 57, 67, 69 and 71 etc. with decreasing amplitudes), the ratio between the peaks of the 28th and 32th masses, which is not characteristic for the air
composition, i.e. probable contribution to the peak of the 28th mass of the synthesized ethylene, indicates the possible initiation of radical plasma-chemical reactions. The reasons for the registration of substances absent both in the initial gas mixture and the background gas may be put down to the possibility of rapid ion-molecule reactions during the residence time \( (10^{-4} \div 10^{-5} \text{ s}) \) of ionized particles in the detector despite the deep vacuum in the mass spectrometric detector.

Methane clusters in the range up to \( m/e = 160 \) are much lower in intensity than the monomeric peaks of hydrocarbon components. Figure 2 shows the relationship between the amplitudes \((\text{CH}_4)_n^+\). Here we show the data for three experiments: pure methane (dark circles); methane makes 80% (gray triangles) and 20% (light gray squares) of the volume, respectively, depending on the \( N \) cluster size. In each mode, the amplitude of the cluster peaks is normalized to the sum of all methane clusters peaks. It should be noted that the comparison presented in Fig. 2, was realized with incomplete coincidence of the gas dynamic parameters of the supersonic jet. To maintain the volume flow of the expiring mixture, we carried through experiments with the same supersonic nozzle and fixed \( P_0 \) and \( T_0 \). With an increase in the proportion of helium in the jet, the productivity of the system's vacuum system decreased. Accordingly, the pressure of the background gas increased, the physical size of the supersonic jet decreased, and the penetration of the background gas onto the axis of the jet increased. The conditions of skimmer interaction also changed.

It can be concluded from the given data that, with a high proportion of methane in the mixture, no significant changes in the distribution of cluster intensities are detected. Some changes begin when the proportion of methane falls below 50%. With further cluster size growth, the rate of amplitude drop will be higher if the methane concentration in the mixture is also higher. In all measurements, the total contribution of the methane oligomers ion peaks is small compared to the monomer amplitude. Nevertheless, it was possible to detect a local maximum at \( N = 6 \). Apparently, this is the first magic number [9] for methane. As expected, methane condensation at moderate pressures and room stagnation temperature is quite inefficient.

It is well known that the van der Waals clusters are fragmented under the influence of the diagnostic electrons of the mass spectrometer. This process proceeds differently for clusters of different sizes and at different energies of ionizing electrons [10-13]. In our measurements, we can assume that methane clusters are effectively destroyed by an electron’s impact, and that rapid ion cluster reactions occur when marked ions are within the detector of the mass spectrometer. There is a slight difference between the amplitudes of the clusters, primarily a slower drop in the amplitude of the ion peaks in the mixture with helium at \( N>6 \). However, it seems that the methane radicals’ ions have a major influence on processes in the region of the oligomers’ mass numbers.

The influence of the buffer gas on the process of methane cluster formation can be estimated by comparing the mass spectra of mixtures of 20%CH\(_4\) + 80%Ar and 20%CH\(_4\) + 80%He, shown in Figure 3. The amplitude of the mass peaks of ions, \( I \), in relative units, is plotted on the ordinate axis. The maximum amplitudes of neighboring peaks are connected by a solid line. The abscissa is the mass number, \( m/e \). For convenience of consideration, the mass spectrum is divided into three parts: \( 1 < m/e < 300 \) - Figure 3(a), \( 288 < m/e < 580 \) - Figure 3(b) and \( 576 < m/e < 900 \) - Figure 3(c).
Figure 3. Comparison of mass spectra in methane mixtures (20% of volume) with buffer gas (80%). Dark lines - buffer gas helium, light lines - argon. The gas-dynamic parameters of both mixtures are the same: $P_0 = 300$ kPa, supersonic nozzle.

In the region $m/e < 160$, the peak amplitudes of the methane cluster ions differ insignificantly in mixtures with Ar and He. With increasing $m/e$, the amplitudes of the mass peaks of methane in a mixture with argon fall sharply to the noise level, while in the mixture with helium they are registered practically throughout the entire dynamic range of the mass spectrometer. It can have several causes. Both buffer gases are reservoirs for absorbing excess energy when forming methane clusters. Helium more effectively participates in this process, perhaps because of the greater average velocity of its atoms. In our experiments, helium, unlike argon, does not condense in a supersonic flow. In the mass spectrum of a mixture with argon, we record small intensity peaks of argon oligomers. Therefore, argon’s own process of condensation can also delay the condensation of methane. In addition, argon is heavier than methane, so its particles displace methane particles from the axis of the jet. As the percentage of helium in the mixture increased, the size and number of methane clusters ion peaks increased as well.

As expected [7], in addition to clusters $(\text{CH}_4)_N^+$, the peaks of protonated methane clusters, $(\text{CH}_4)_N\cdot\text{CH}_3^+$, are recorded in mass spectra. The amplitude of the protonated peaks increases with the growth of the mass number. Peaks of clusters with an attached methyl group $(\text{CH}_4)_N\cdot\text{CH}^+$ were also detected in the mass spectrum. In addition to $N = 6$, the local maximums of the amplitudes are recorded on mass peaks corresponding to the sizes of clusters $N = 14, 23, 36, 44$, which also can be magical numbers for methane clusters.
4. Conclusions
With identical gas-dynamic parameters, the processes of methane clusters’ formation in a medium of condensing argon and non-condensable helium were compared. It is shown that the process of methane condensation depends on the choice of the carrier gas, its properties and the volume fraction of methane in the mixture for the given gas dynamic parameters of the flow. A wide spectrum of cluster methane ions, protonated cluster methane ions, as well as an increase in the intensity of cluster peaks of methane of large masses with a decrease in the percentage of methane in helium were registered. The effect of methane dissociative ionization and methane clusters fragmentation in the mass spectrometer detector on the registered composition of clusters is established. Magic numbers for methane clusters are found.

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References
[1] Schauer M, Law K and Bernstein E R 1984 J. Chem. Phys. 81 49
[2] Wachtendorf C, Herweg C, Daeuber M, Benedikt J and von Keudell A 2009 J. Phys. D Appl. Phys. 42 095205
[3] Milani P, Barborini E, Piseri P, Bottani C E, Ferrari A C and Li Bassi A 1999 Eur. Phys. J. D 9 63–8
[4] Lu H, Chen G, Ni G and Xu Z 2010 J. Phys. Chem. A 114 2-9
[5] Li S, Lu H, Zhang H, Nakajima K, Liu J and Ni G 2013 Chinese Opt. Let. 11 (Suppl) S20201A
[6] Yang S, Philippe L and Châtelet M 2007 Internat. J. Mass Spectr. 263 190-94
[7] Zarvin A E, Kalyada V V, Korobeishchikov N G and Khodakov M D 2014 Nanoengineering (in Russian) 31 3-6
[8] Zarvin A E, Kalyada V V, Madirbaev V Zh, Korobeishchikov N G, Khodakov M D, Yaskin A S, Khudozhitkov V E and Gimelshein S F 2017 IEEE Transact. Plas. Sci. 45 819-27
[9] Schütte S and Buck U 2002 Intern. J. Mass Spectr. 220 183-92
[10] Echt O, Fiegela T, Rümmele M, Probst M, Matt-Leubner S, Urban J, Mach P, Leszczynski J, Scheier P and Märk T D 2005 J. Chem. Phys. 123 084313
[11] Bonhommeau D, Halberstadt N and Viel A 2006 J. Chem. Phys. 124 184314
[12] Zhang P, et al 2014 J. Phys. Conf. Ser. 488 052032
[13] Eletskii A V and Smirnov B M 1989 Sov. Phys. Usp. 32 763-82