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Mass spectrometric study of gas clusters by a high-voltage electron beam

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Annotation. The possibility of using a high-voltage electron beam as an ionizer of supersonic clusters of argon and methane gas jets in molecular beam mass spectrometry are investigated. The formation of clusters occurs when the gas flows through the supersonic nozzle into the vacuum. The ionization of the flow is carried out by electrons with an energy of 10 keV. The diaphragm (skimmer) from jet forms a molecular beam, which passes into the input aperture of the mass spectrometer through the sections of the installation. The ion focusing is provided with the use of collimating diaphragms as electrostatic lenses. A quadrupole mass spectrometer is used as a cluster ion analyzer. The obtained mass spectra are compared with the signals observed with the usage of traditional molecular beam mass spectrometry, in which ionization of particles occurs in the electron analyzer's own block with energies of the 100 eV order. The justification of the standard approach shortcomings is proposed. Obtained data shows chemical reactions in hydrocarbons and cluster magic numbers for argon, obtained result is consistent with known data.

Mass spectrometry is an effective method of studying substances. This tool is suitable for the analysis of Van der Waals gas clusters, since the received signals allow us to directly consider the composition of the clustered gas jets, allowing us to track the reactions of synthesis and fragmentation of particles that are the main subject of cluster research. The traditional molecular beam mass-spectrometry technique assumes the following stages: the formation of an object - a supersonic jet, the extraction of a molecular beam, the transport of a stream to an analyzer, the ionization and recording of signals. However, the investigation of van der Waals clusters in supersonic flows requires special conditions for carrying out such experiments for a number of reasons.

First, for quadrupole mass spectrometers, there are limitations on the mass composition of the investigated substances [1]. The focusing system of analyzers is designed to receive particles with the same phase volume. But when electron impacts on particles, both direct and dissociative ionization are possible. The energies of ions with the same mass will differ significantly depending on the type of charging. Hence, there could be significant losses of signals for small masses, in comparison with large ones. One of the features of cluster flows is the wide size distribution, this effect results in distortion of the received signals.

Secondly, electron ionization of gas clusters leads to their effective fragmentation into smaller parts [2]. This is due to the low values of the binding energy of van der Waals particles in comparison with atoms or molecules. Multiple ionization creates an uncompensated charge, leading to the destruction of associates to elements of an arbitrary size under the influence of Coulomb forces. In addition, the
energy of electrons ionizing neutral particles in the most of the mass spectrometers blocks is usually chosen near the maximum ionization cross section of most atoms and molecules (40-70 eV), It is much larger than the binding energy of gas clusters. Therefore, it is advisable to use high-energy electrons to reduce the collision times of electrons with particles and lower the possibility of multiple interactions.

Thirdly, the process of formation of a molecular beam can exert additional influence on the resulting signals, that was observed when tracking monomer signals in [3]. Because the velocity ratio has a proportional dependence on the particle mass, a dependence of the cluster size on the distance to the beam axis is formed. Cutting a narrow part of the jet with a skimmer results in the selection of large clusters.

All these factors have to be taken into account when analyzing gas clusters by molecular beam mass spectrometry. In this paper, we investigated the possibility of reducing the distortion of a neutral flow by using a configuration with an external high-energy ionizer. The experimental gases argon and methane were selected from the following considerations: argon is well-studied object in plasmachemistry as it has good condensation ability, in methane mixtures it is possible to conduct multiple plasma-chemical reactions. The work was performed on the experimental gas-dynamic complex "LEMPUS-2" NSU [4]. The scheme of experiments is shown in figure 1. Gas clusters were formed due to adiabatic expansion of the gas from the pre-chamber (1) through the nozzle into the expansion section (2). A molecular beam was emitted by a skimmer (3) with a diameter of 0.46 mm and angles of 40° x 50°. The selected flow was delivered through the post-skimmer section (4), collimated with a diaphragm (5) with a diameter of 3 mm, and then in the detector section (6) it reached the diaphragm of the quadrupole mass spectrometer Hiden EPIC 1000 (7). The ionization of the flow (8) was carried out by a high-voltage focused electron beam (9) with an electron energy of 10 keV. The electron source was an electron gun with a hollow cathode. Extraction of ions and subsequent transportation to the analyzer was provided by electrostatic lenses - diaphragms. In a standard configuration, the gas was ionized inside the mass spectrometer by its own block with the electron energy of 70 eV.

The experiments were provided on argon with the sonic nozzle of 0.55 mm in diameter and on methane with the supersonic nozzle of 0.215 – 17 – 3,8 mm (the critical section diameter - length of the diffuser - the outlet section diameter). The temperature of the gases in the pre-chamber of the nozzle is 298 K. The change in the pressure in the nozzle pre-chamber, P₀, provided a variation in the average particle size, <N> (unit / cluster), calculated by Hagen's formulas [5]. The formation of a molecular beam from a jet was carried with minimizing the influence of the skimmer and shock waves by changing the nozzle-skimmer distance.

Figure 1. The scheme of experiments. 1 – pre-chamber of nozzle; 2, 4, 6 - expansion, post-skimmer and detector section, respectively; 3 - skimmer; 5 - collimating diaphragm; 7 - mass spectrometer; 8 - flowing gas stream; 9 - electron beam
In figure 2 a comparison is made of the percentage composition of the detected argon clusters at several pressure values $P_0$ (with the corresponding estimated values of $<N>$) in the two ionization variants. To compare the amplitudes of cluster peaks I as a function of their size N, the data are divided by the total intensity. It can be seen that the usage of a high-voltage electron beam to ionize the jet and the further transport of ions to the detector of the mass spectrometer (solid markers) ensure the delivery of a larger number of cluster ions than in the standard version (empty markers). Also there are observed regular singularities in the case of ionization by an electron beam at $m/e = 11, 19, 21$, which coincide with data on magic cluster numbers in argon [6]. Consequently, a configuration with an external ionizer gives more informative results.

The growth of the braking pressure leads to an expansion of the recorded mass spectrum toward larger clusters. In modes with a high-voltage electron beam, there is also a tendency to reduce the difference in the amplitude of the peaks of monomers and small clusters, illustrated in figure 3. This result correlates with the idea of cluster size growth with increasing inhibitory pressure [5]. However, the maximum intensity at all pressures $P_0$ remains for the monomer signal.

**Figure 2.** Percentage composition of recorded mass spectra for different $P_0$ (kPa) and $<N>$. Empty markers - ionization inside the mass spectrometer, solid - in the supersonic jet.

**Figure 3.** $(\text{Ar})_N/\text{Ar}^+$ Signal ratio for dimers (2), trimers (3), and tetramers (4) for various average particle sizes $<N>$. 

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Unlike argon, the initiation of chemical processes is possible for methane. Therefore, it makes sense to consider the resulting clusters taking into account possible chemical transformations, the conditions of which can differ greatly in the selected measurement regimes. For this, all possible associations variants were registered.

When mass spectra were recorded, it was found that the background peaks of water vapor present in the mass spectrum (m/e = 18 and 17) in the case of ionization in a jet by a high-voltage electron beam are lower in amplitude than hydrocarbon signals. On the contrary, they are larger when ionization occurs inside the mass spectrometer. Since there is practically no water vapor in the detector section of the mass spectrometer due to low background pressure (less than 10^{-5} Pa in all measurement regimes), the presence of water peaks in the recorded spectra is explained by the penetration of the background gas into a supersonic jet. Ionization of the flow occurs at a much closer to the nozzle distance than the skimmer. To suppress interference, it is desirable to have a high density of neutral condensed particles. At the same time, the selection of a molecular beam with a skimmer is performed at a low flux density to avoid a skimmer interaction distorting the flow parameters, i.e., as far as possible from the nozzle. Penetration of the background gas into the jet increases downstream. Thus, the use of external ionization has the advantage in reducing the noise level.

The amplitudes of the signals of the clusters in the pure methane streams with the standard configuration turned out to be comparable with the error. These mass spectra changed only slightly with the changing of the pressure in the nozzle pre-chamber, in contrast to the results using an electron beam. In order to increase the proportion of the condensate, mixtures of methane and helium were used. Non-condensing helium provided absorption of methane condensation energy. A comparison of the mass spectra of methane in a mixture of 40% CH4 + 60% He with two ionization variants is shown in figure 4. For convenience, not mass peaks are given, but their maximum amplitudes connected by solid lines.

As expected, the dependencies obtained have significant differences in the educated chemical groups. In the case of ionization by a high-voltage electron beam, clusters of the oligomeric series are detected as well as (CH₄)ₙ₋₁(CH₅)⁺ and (CH₄)ₙ₋₁(CH⁺), whereas in standard ionization cluster peaks are poorly noticeable (typical hydrocarbon series peaks m/e, 27 and 29, 41 and 43, 55 and 57, 67, 69 and 71, etc.), and the signals (CH₄)ₙ₋₁(CH₅)⁺ and (CH₄)ₙ₋₁(CH₃)⁺.

The results of this work demonstrate, first of all, the advantages of using external ionization in molecular-beam gas cluster mass spectrometry. Also, the shortcomings of the standard configuration with illustrative examples are explained. The features of the formation of clusters of various gases are noted, and chemical reactions in hydrocarbons are detected.

Figure 4. Percentage composition of the mass spectra of methane ionized in the detector of the mass spectrometer and in the expansion chamber with the addition of 60% helium (P₀ = 400 kPa).
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