Experimental study of the fragmentation of van der Waals gas clusters by electron ionization

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Abstract. The fragmentation of gas clusters of argon, nitrogen and methane during ionization by electron impact have been examined. Clusters were formed when the gas flowed through the supersonic nozzle into the vacuum. A molecular beam was selected from the supersonic jet by the skimmer, then it reached the analyzer of the quadrupole mass spectrometer Hiden Epic 1000. The ionization of the gas was carried out in the molecular beam by the intrinsic ionizer of the detector with an electron energy of 70 eV and in the supersonic jet by an electron beam (10 keV). A comparison of mass spectra obtained by both methods with different parameters of the supersonic jet has been done. The difference of the obtained cluster distribution has been substantiated; the disadvantages of using the classical configuration of quadrupole mass spectrometry have been analyzed. Dependences of the percentage composition of the recorded flows have been obtained. Distinctive "magic" cluster numbers have been found.

Cluster is considered to be a composition of atoms or molecules located in a state between a molecule and a solid [1]. The use of these particles lies in a wide range: from polishing surfaces to creating organic structures. The most common method of creating gas clusters is the use of gas flowed into the vacuum through sound or supersonic nozzles. Such adiabatic expansion of the flow leads to the formation of associates within which the particles are retained by van der Waals forces and have a wide size distribution. Since the study of clusters and their characteristics involve consideration of the composition of jets, one of the best approaches to the study of these objects is the ionization of clusters with subsequent detection of the flow by a mass spectrometer. However, the application of this technique requires special conditions for analysis due to a number of reasons.

Firstly, quadrupole mass spectrometers discriminate particles by mass [2]. This happens because the energies of the ionized particles and the energies of the fragments detached from them can vary greatly. At the same time, focus parameters are calculated for the particles with the same energy. Therefore, the difference in the phase volumes of identical particles leads to signal losses. So it can significantly affect the correctness of the different masses signals ratio for cluster flows with a wide size distribution.

Secondly, it is known from the literature [1, 3–5] that one of the features of gas clusters is their intense fragmentation during the electron ionization. Multiple ionization results in the appearance of Coulomb repulsion that in turn leads to the collapse of the cluster into fragments the size of which can vary greatly. On the other hand, the electron energy used in ionizers of quadrupole mass spectrometers usually lies in the region of 40–70 eV that corresponds to the maximum ionization cross section of most molecules and considerably exceeds the binding energy of van der Waals associates. So, if the
task is to analyze the composition of cluster flows, it is better to increase electron energies in order to reduce the fragmentation effect by decreasing the time of collisions.

In addition, it is worth mentioning the distortion possibility of the recorded flow due to the effect of jet selection [6]. This feature is connected to the fact that the velocity ratio is proportional to the mass of the particle. This results in the dependence of the particle masses on the distance to the axis of the jet. Therefore, the selection of the axile part by the narrow skimmer for the purpose of forming a molecular beam, that is used in the most configurations for flow analysis, facilitates the selection of large clusters. Thus, it is necessary to take into account these features when analyzing gas clusters.

The study was performed on an experimental gas-dynamical assembly LEMPUS-2 at Novosibirsk State University [7]. The scheme of experiments is shown in figure 1.

Clusters were formed when the gas flowed from the nozzle supply (1) through the sound or supersonic nozzle into the extension chamber (2). A molecular beam was selected by the skimmer (3) with the diameter of 0.44 mm and the angles of 40–45° and then through the section after the skimmer (4), the collimating diaphragm 3 mm in diameter (5) and the detector section (6) reached the input aperture of the mass spectrometer (7) with the diameter of 4 mm. The gas flow (8) was ionized in the expansion chamber by the high voltage (10 keV) electron beam (9) the source of which was an electron gun with a hollow cathode or the intrinsic ionizer of the mass spectrometer with the electron energy of 70 eV. In the first case the skimmer and the collimator were used as electrostatic lenses in order to minimize ion losses during the transport of charged clusters along the assembly to the detector, a series of experiments is provided to optimize the delivery of ions. The quadrupole mass spectrometer Hiden Analytical EPIC 1000 which can make records in the range from 1 to 1000 a.m.u., was used in this work. According to the received mass spectra, the sensitivity of the instrument is 7 orders of magnitude. The pressure in the nozzle supply $P_0$ ranged from 21 to 500 kPa.

Experiments with the sound nozzle 0.55 mm in diameter on argon and with the supersonic nozzle of 0.17-8.2-2.2 and 0.215-17-3.8 (the diameter of the critical section – the length of the diffuser - the diameter of the outlet section) on methane and nitrogen were carried out. The gas temperature in the pre-chamber in the experiments was 298 ± 1 K. The formation of the molecular beam was in the region of absence of both skimmer effect and the influence of the Mach disk to avoid the gas dynamics distortion of the flow. The choice of the sound nozzle for the analysis of argon clusters is caused by the large average sizes $<N>$ of neutral clusters (calculated by the Hagen's formulae [8]) in comparison with nitrogen and methane. In order to increase the amount of condensate in the jets of methane, helium was added in various proportions.

The comparison of the mass spectra of argon at $P_0 = 100$ kPa (average cluster size $<N> = 25$) is shown in figure 2. The mass spectrum obtained as a result of supersonic jet ionization (blue markers...
e-b) shows modal distribution behaviour. In this case the amplitudes of the cluster peaks are quantitatively higher than the values obtained during ionization by the intrinsic block. Consequently, the use of the high voltage electron beam gives more informative signals. This result is also confirmed with other values of stagnation pressure, i.e. with other average cluster size.

Figure 2. Comparison of the mass spectra of argon clusters during different ionizations: red – ionization in the mass spectrometer; blue – ionization in the expansion section.

Figure 3 shows the percentage ratios of amplitudes of the recorded clusters depending on their size N for three different stagnation pressures, respectively, for the three average cluster sizes calculated by the formula of O. Hagena [8]. At the same time, an increase of <N> resulted in not only to the broadening of the distribution in the direction of large masses but also to the significant reduction of the ratio of the amplitudes between the signals of the monomers and other small clusters; that corresponds to the concept of the distributions behaviour when the pressure changes. Interestingly, the presence of regular singularities for m/e = 11, 14, 19 and 21 that coincides with the data on argon “magic” cluster numbers [9]. However, the monomer signal remained predominant for the selected pressure range.

Figure 3. Percentage composition of the recorded mass spectra for different P₀ and, respectively, values of <N>: dashed lines – ionization of the molecular beam; solid lines – ionization of the jet.

Another result is observed when nitrogen jets flow in the conditions of large clusters formation. Figure 4 shows the data obtained at stagnation pressure P₀ = 400 kPa. In this mode the evaluation according to the parameter of O. Hagena gives an average cluster size of <N> = 254. The mass spectrum recorded by the intrinsic ionizer of the mass spectrometer, figure 4(a), consists of a monomer signal (m/e = 28) that is almost three orders of magnitude smaller than a dimer signal (m/e = 56) and is about an order of magnitude smaller in the amplitude of the group of oligomers from 6 to 12 (m/e from 168 to 336).

In the case of ionization by the high voltage electron beam, figure 4(b), a set of cluster peaks is much larger in amplitude and composition. The maximum amplitude of the signal is recorded on
hexamers of nitrogen; the amplitude of the monomers is smaller than the one of the clusters, from dimers to hexamers inclusive. This is completely different from the spectrum of the device's intrinsic block. The change of the stagnation pressure results in the displacement of the maximum peak towards larger or smaller masses which is not observed with the standard configuration of the ionizer. Also a group of peaks at N = 24 and above is recorded in the mass spectrum. Signals on these masses have a small amplitude and cannot be regarded as reliable.

![Figure 4](image)

**Figure 4.** Mass spectra of nitrogen clusters ionized in the detector of the mass spectrometer (a) and in the expansion chamber (b), P$_0$ = 400 kPa, $<$N$>$ = 254.

Several local maxima are also observed in the mass spectrum recorded during ionization by high voltage electrons in the jet. As it is observed in figure 4(b), at a pressure P$_0$ = 400 kPa the maxima are at m/e = 56, 168 and 280 a.m.u. that corresponds to the cluster size N = 2, 6, and 10. The measurements at variations of the stagnation pressure proved that the size of the clusters with absolute or local maximum of the amplitude shifts. The number of recorded clusters of a larger size also changes.

The dependence of the value of the size of clusters with absolute or local maximum of the amplitude on the stagnation pressure is shown in Table 1.

| N   | P$_0$, kPa | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|-----|------------|---|---|---|---|---|---|---|---|---|----|----|----|
|     |            | 1 |   |   |   |   |   |   |   |   |    |    |    |
| 100 | A          |   |   |   |   |   |   |   |   |   |    |    |    |
| 200 | A          |   |   |   |   |   |   |   |   |   |    |    |    |
| 300 | L          |   |   |   |   |   |   |   |   | A  |    |    |    |
| 400 | L          |   |   |   |   |   |   |   |   | A  | L  |    |    |
| 500 | L          |   |   |   |   |   |   |   | L  |   | A  |    |    |
| 600 | L          |   |   |   |   |   |   |   | L  |   |    | A  |    |
Results that have been obtained in molecular nitrogen during ionization in the jet by a high voltage electron beam on "half" masses have been formed as a result of dissociative ionization of molecular nitrogen and its clusters are also interesting. The obtained mass spectrum at recording of all peaks with nonzero amplitude at stagnation pressure $P_0 = 500$ kPa is shown in figure 5. It is noticeable that the amplitudes of the peaks $(N_2)_n N^+$ are less than $(N_2)_n^+$ for all values of $n$, except $n = 2$, at the same time, when $n$ grows, the ratio first increases to 40-fold but then decreases to 20-fold.

Undoubtedly, the processes of interaction of ions and neutral particles on the path from the site of ionization to the ion detector have a great impact in such difference of the results using different methods of ionization, that was also noted by other authors [2–3, 10]. Also it can be assumed that the effect obtained in nitrogen jets unlike argon can be caused by the physical features of molecular clusters in comparison with the atomic ones. In addition, it is possible that there is influence of volume charge compensation by negative nitrogen ions during the transportation of ions formed by the high voltage electron beam in the jet to the detector of the mass spectrometer.

The results of this study demonstrate the possibilities and advantages of using external ionization in the molecular beam cluster gas mass spectrometry.

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