



Short communication

Simple method to gas cluster size determination based on molecular beam cross-section



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ABSTRACT

A new experimental method of gas cluster size determination based on measuring the transverse profile of the total intensity of a molecular beam was developed. Since the supersonic beam has a high intensity, the proposed method not requires high-sensitivity detecting equipment. By using this method it can determine the mean cluster size *in situ* not only of any pure gases, but in gas mixtures under certain conditions as well. Experimental measurements were carried out in jets of pure gases (Ar, CO₂, N₂) and gas mixture (10% C₂H₄ + 90% He) expansions through supersonic conical nozzles. The Hagen scaling parameter of the source conditions Γ^* varied from 10^2 to 2×10^4 . The mean cluster sizes defined by new method were in the range of 50–1500 molecules/cluster. Comparison of the experimental data to the results of numerical simulations and estimates using the empirical formulae developed elsewhere shows a satisfactory agreement.

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Cluster size is one of the most important characteristics that determines the properties of gas clusters, such as phase state of cluster substance, energy transfer processes, of interaction between cluster and solid etc. Basic experimental methods of gas cluster size determination can be divided into conditionally direct mass-spectrometer measurements [1,2], and scattering methods, such as the scattering of cluster beam itself (buffer gas [3,4] or crossed molecular beam scattering [5]), or scattering of the external flow on the cluster beam (i.e. Rayleigh scattering [6–8], electron diffraction [9], X-ray diffraction [10], etc.). All mass spectrometer measurements are based either on electron impact or photon ionization of neutral clusters. Since the binding energy of particles in a cluster is, as a rule, lower than the ionization threshold energy, it could obviously result in the cluster fragmentation. The fragmentation processes as well as discrimination during transportation and detection of heavy ions can lead to distortion of the recorded cluster ion mass-spectra compared to the initial sizes of the neutral clusters. Scattering methods of cluster size measurements provide correct measurement of clusters of large size mostly, and, additionally, they require development and verification of special models for the utilized scattering mechanisms, and for every particular gas. In all known methods of cluster size determination,

it is the cluster density in gas flow that is being measured. Small sizes and instability of gas clusters due to low binding energy determine the difficulty of this task and require complex high-sensitivity equipment for such measurements. As a result, there are still many experimental works being carried out, and investigation of numerical models for the development of methods for the cluster sizes determination is ongoing [11–14].

The present paper describes a new experimental method for determination of cluster sizes in molecular beams of any pure gas, and even under certain conditions, in gas mixtures. This method is based on measuring the transverse intensity profile of a molecular beam. It is known that in a free jet, behind the sonic nozzle in the absence of influence of background gas the flow is similar to the radial expansion from a virtual point source [15]. It has been shown that the flow of a condensable gas through supersonic nozzles can also be characterized by radial expansion within the small effective angle θ_{eff} . The spatial distribution is limited by the increase of the boundary layer on the nozzle walls; therefore the value of θ_{eff} is noticeably smaller than the geometric angle of the cone θ [16]. Passing through the skimmer, provided there are no collisions between particles at the entrance of the skimmer ($Kn_{sk} > 1$) and no collision with the background gas behind the skimmer, the flow will turn into free-molecular expansion mode. The degree of gas spread (i.e. the relationship between the longitudinal coordinate, directed along the axis of symmetry of the beam, and the perpendicular coordinates of the particles) is characterized by the

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speed ratio of flow S :

$$S = \frac{U}{V} = \left(\frac{m^* U^2}{2k^* T} \right)^{1/2} \quad (1)$$

where m is the mass of particles, U is hydrodynamic velocity of the flow, V is a mean thermal velocity for gas temperature T , and k is the Boltzmann constant. In the case of mixture beams, the difference in magnitude of the speed ratios results in the well-known Mach-number focusing effect: enrichment of the beam centerline with heavy particles [17].

It is obvious that spatial separation also appears in the beam, consisting of both monomers and clusters of different masses. Behind the skimmer, monomers and small clusters (oligomers) spread in a larger solid angle than heavy clusters. This leads to a significant increase in the relative fraction of clusters at the beam centreline. This then results in the beam intensity on the axis being provided mainly by the clusters at a great distance from the skimmer, although the gas flow at the entrance to the skimmer mostly consists of monomers (the condensate mass fraction q typically does not exceed 30%) [18]:

$$I_{cl-b} \approx n_{sk}^* V^* d_{sk}^2 * q^* N^* S_1^2 \quad (2)$$

where n_{sk} is the density of the gas flow at the entrance to the skimmer and S_1 is the speed ratio of monomers.

As the gas expands from a point source, the diameter of molecular beam d_b at a distance L downstream from the skimmer is summed up by the “geometric” diameter d_g (determined by the solid angle of the skimmer) and the beam broadening Δ occurring due to free-molecular thermal spreading of particles with speed ratio S :

$$d_b = d_g + \Delta \approx d_g + L/S \quad (3)$$

The cluster beam with a mean size N is characterized by a speed ratio S_N , and in conditions of thermal equilibrium between monomers and clusters in the jet we obtain $S_N = \sqrt{N}^* S_1$. Apparently, the broadening of the cluster component of the beam is considerably smaller than the monomer flow broadening:

$$\Delta_1/\Delta_N = S_N/S_1 = N^{1/2} \quad (4)$$

Thus, by measuring the broadening of the monomer and the cluster components of the beam at a fixed distance behind the skimmer L , we can calculate the corresponding speed ratios S_1 and S_N and, as a result, determine the mean cluster size for the given conditions. Since the clusters in supersonic jet have a very broad size distribution and are spread at different angles, the mean cluster size is characterized by the half-width (i.e. the width at the half-height) of the cluster flow components.

The direct relationship between the width of the molecular beam and the speed ratio of particles has already been noted elsewhere (e.g. [18]). However, no practical implementation of our method of gas cluster size determination is known to us. Earlier, the method for determining the translational temperature of the gas flow was realized on the basis of measurements of transverse density profiles of molecular beam [19]. The approach most similar to our method was used in [20], where cluster sizes were calculated using the broadening of the beam after it passed through the buffer gas. However, this method can determine the sizes of large ($N > 10^3$) clusters generally. Complex equipment and empirical constants that depend on the gas nature are required to analyze the measurement results. Beam density profiles were measured in both works, and such measurements require a high sensitivity of

detecting equipment. Since the supersonic beam has a high intensity, a standard ionization pressure sensor was used as a detector for measurements in the proposed method.

The experiments were carried out with a 10 mm long conical nozzle with throat diameter $d^* = 0.28$ mm and half-angle of 6° , and skimmers had the inlet diameters $d_{sk} = 0.43$ and 0.83 mm. In all described regimes the distance between the nozzle and the skimmer was 50 mm. The transverse profile of the total (mass) beam intensity was measured by moving the closed detector perpendicular to the axis of the molecular beam using a linear manipulator. At the input of the detector, a 1.2 mm width slit aperture was set perpendicular to the axis of motion to ensure the spatial locality of measurements. Measurements were performed in pure gases and gas mixture at different distances between the skimmer and the detector L_{sk-det} ; stagnation pressures varied from $2 \cdot 10^4$ to $7 \cdot 10^5$ Pa, stagnation temperature was 300 K. The technique of measurement of total intensity of the cluster beams was described previously [21].

Fig. 1 shows the profiles of the total intensity of the molecular beam I_{total} (mol/(cm²*s)), measured in jets of different gases under the same conditions. Since we used an ionization intensity sensor, differences of the ionization cross-sections of various molecules were taken into account to compare the intensity of various gases. Under these conditions, the clusters were not detected in nitrogen, and the cross-section has a wide profile, corresponding to the distribution of monomers with an intensity that monotonically decreases from the centerline. A characteristic bimodal distribution appears in all gases in the presence of clusters. The narrow peak formed by the distribution of clusters in the flow is recorded near the beam centerline beside the wide profile of monomers. In the case of gas mixture expansion, helium acts as a carrier gas, setting the flow dynamics, transferring the heat of condensation but not forming clusters. Ethylene forms clusters intensively due to its good polymerization and effective gas flow cooling by helium. As a result, the beam intensity in the mixture is significantly higher than the intensity in pure gases. In the mixture, the half-width of the cluster peak is noticeably larger than the half-width of the cluster peaks in pure gases.

The beam cross sections, recorded in argon at different pressures P_0 , are shown in Fig. 2a. In Fig. 2b, the same cross section is normalized to unity at the maximum of total intensity. For low stagnation pressures it can be seen that the profile has a large half-width, which characterizes the intensity distribution in a divergent flow of monomers. With P_0 increasing, the total beam intensity on

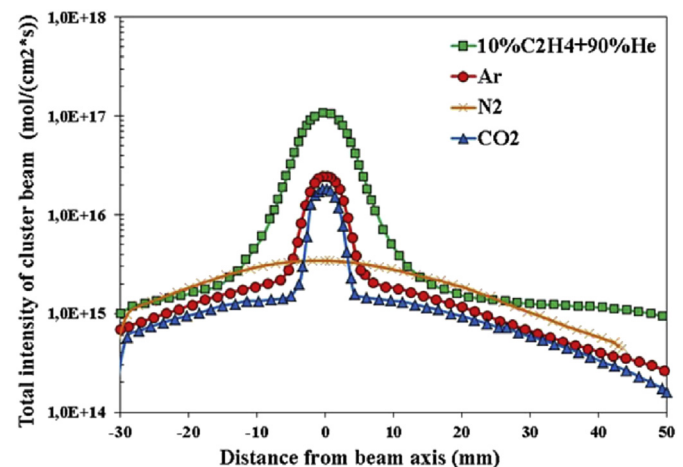


Fig. 1. Cross-section of cluster beam total intensity in different gases at the same conditions: $d_{sk} = 0.83$ mm, $L_{sk-det} = 321$ mm, $P_0 = 2 \cdot 10^5$ Pa.

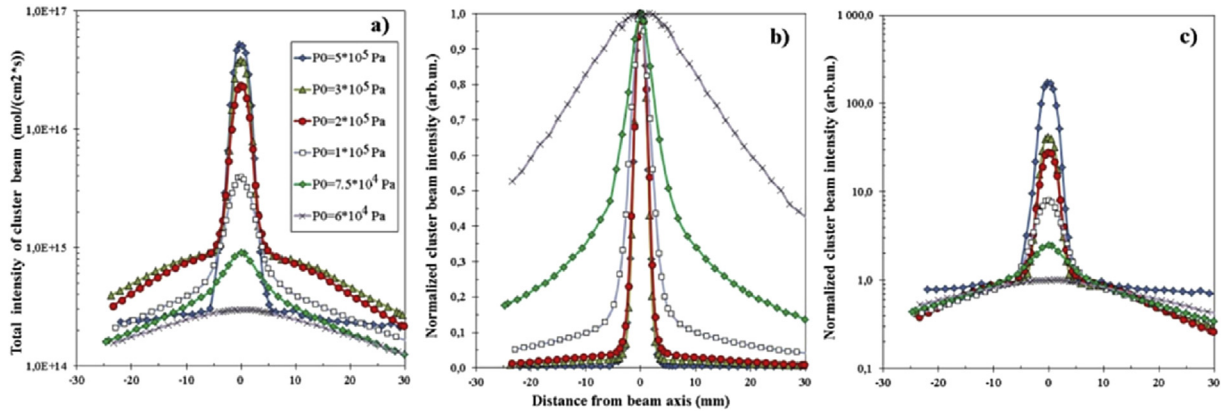


Fig. 2. Cross-sections of cluster beam intensity in Ar for various stagnation pressures at $d_{sk} = 0.43$ mm, $L_{sk-det} = 321$ mm: (a) total intensity, (b) intensity normalized at maximum of signal, (c) intensity normalized at maximum of monomer component.

the axis dramatically increases too: by increasing the stagnation pressure from $4 \cdot 10^4$ to $3 \cdot 10^5$ Pa, the intensity on the beam axis increases by almost 2 orders of magnitude. At the same time the intensity of the monomer component increases less than 3 times. This confirms the fact that under the conditions of developed condensation at a great distance behind the skimmer predominantly large clusters are concentrated on the beam axis, providing the main contribution to the measured value. For example, in these conditions for $P_0 = 3 \cdot 10^5$ Pa, the ratio between the intensities of the monomer and the cluster components on the beam axis is $I_{mono}/I_{clust} \sim 0.05$. It was found that starting with the pressure of $2 \cdot 10^5$ Pa the half-width of the cluster peak profile almost does not change (see Fig. 2b). For $P_0 > 2 \cdot 10^5$ Pa on the selected path length $L_{sk-det} = 321$ mm, the broadening of the cluster component is small, so within the measurement error the geometric half-width of the beam agrees with the half-width of the cluster component and equals $d_g = 2.8$ mm. The geometric width of a beam can be determined in a similar way for other conditions. It is obvious that the value of d_g changes if any geometric parameter changes: i.e. the nozzle-skimmer distance, skimmer diameter or skimmer-detector distance.

Fig. 2c shows the same profiles, but normalized to unity on the axis of the monomer component of the beam. As can be seen, the half-width of the profile of the monomer component changes but only slightly, with increasing stagnation pressure, except for $P_0 = 5 \cdot 10^5$ and $6 \cdot 10^5$ Pa. It was found that in the case of the argon flow the jet dimensions reduce, starting with $P_0 = 5 \cdot 10^5$ Pa, due to the increase of the background pressure in the expansion chamber. For $P_0 = 5 \cdot 10^5$ Pa the profile was measured at the jet edge in front of a X-shaped shock wave, and for $P_0 = 6 \cdot 10^5$ Pa it was measured behind the shock waves [21]. Primarily the impact of the shock wave is manifested most significantly in the broadening of the profile of the monomer component, which is the result of the drop in speed ratio of monomers S_i . After passing through a shock wave, the clusters evaporate partially (i.e. the mean size decreases), which leads to a drastic drop in the intensity of the cluster component on the beam axis (see profile for $P_0 = 6 \cdot 10^5$ Pa).

Because the broadening of the cluster component is insignificant for a small path length, in order to determine the size of large clusters the measurements were made at large skimmer-detector distances. Fig. 3 shows the transverse total intensity profiles, measured at $P_0 = 2 \cdot 10^5$ Pa at different skimmer-detector distances L_{sk-det} . As expected, when the distance increased, the total intensity of the beam decreased, and the half-width profile of both the cluster and the monomer components monotonically increased. In addition, the intensity of the monomer component on the flow axis

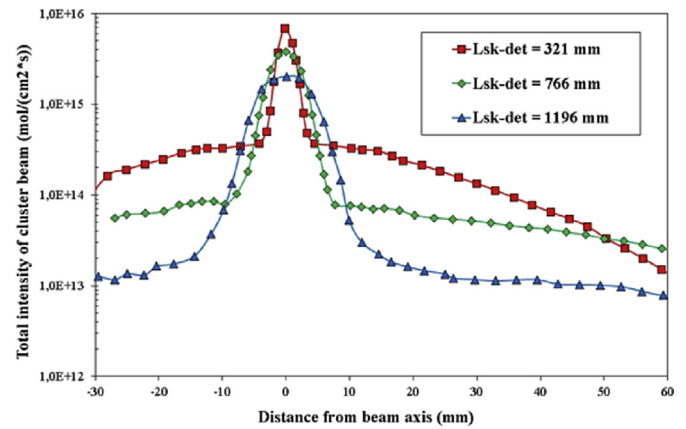


Fig. 3. Cross-section of cluster beam intensity in CO_2 at $P_0 = 2 \cdot 10^5$ Pa, $d_{sk} = 0.83$ mm for various skimmer – detector distance L_{sk-det} .

reduces according to the known dependence for the molecular beam $I_{mono} \approx 1/L_{sk-det}^2$ [15], whereas the intensity of the cluster component is reduces much less quickly $I_{clust} \sim 1/L_{sk-det}$. Background gas scattering leads to some additional broadening of the beam.

It is known that with increasing stagnation pressure, the condensate mass fraction approaches its limit, the mean size of clusters continues to grow, but the numerical intensity may even decrease [21]. The formation and growth of clusters leads to a reduction of the local gas density and a corresponding decrease in the number of collisions downstream. With increasing P_0 , the number of condensation nuclei increases. But the small clusters do not have time to grow into a large size, which leads to the increase in their number in the far field of the flow.

Using the experimental results, the mean cluster size was calculated for pure gases and the mixture. The corresponding value of scaling parameter [22] Γ^* is indicated for each mode. Values of the mean cluster size listed in the Table 1 were obtained by numerical calculations using the model [21] and common empirical formulae [5,22]. Only experimental results are presented for gas mixture since the necessary empirical coefficients and tested numerical models are missing. It can be seen that the cluster size data obtained in the experiment are in satisfactory agreement with numerical calculations and empirical formulae estimates. The results obtained by the formula [22] are the only exception, with high Γ^* parameters producing overestimated values of cluster sizes, as

Table 1

Mean cluster size N vs Hagen scaling parameter Γ^* for different gases. Exp – experimental data obtained in this work; sim – results of numerical simulation, calc – results of estimates using the empirical formulae.

P_0 (bar)	0.4	0.6	0.75	1.0	2.0
Ar					
Γ^*	9.1×10^2	1.4×10^3	1.7×10^3	2.3×10^3	4.5×10^3
N , exp	—	60	75	140	565
N , sim	24	74	91	138	320
N , calc ^a	33	64	92	227	1156
N , calc ^b	33	64	82	178	647
CO ₂					
Γ^*	2.0×10^3	3.0×10^3	3.8×10^3	5.0×10^3	1.0×10^4
N , exp	71	270	340	510	1490
N , sim	70	148	235	393	1315
N , calc ^a	121	236	750	1475	7512
N , calc ^b	144	306	462	748	2757
10% C ₂ H ₄ + 90% He					
N , exp ^a	105	280	770	—	—

^a Reference [22].

^b Reference [5].

confirmed elsewhere [8]. At the same conditions, the maximum cluster size is recorded in mixture. The minimum size of clusters that can be determined by this method is determined by the ratio of the intensity of the cluster and the monomer components, i.e. the sensitivity of the detector. To determine the size of large clusters it is necessary to increase the path length in the absence of the influence of the background gas at the cross-section of the beam.

In conclusion, a new experimental method for determination of the mean cluster size in molecular beam has been approved. The approach is based on recording the cross-section of the total intensity profile of the beam, and the determination of the half-widths of the cluster and the monomer components of the flow. Due to the high intensity of the cluster beam, this method does not require any complex high-sensitivity equipment and can actually determine the mean cluster size *in situ* not only in supersonic jets of any pure gases, but in gas mixtures under certain conditions as well. The mean size of small ($N = 50$ – 100) and medium-sized ($N = 100$ – 1000) clusters can be easily determined using this method.

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