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Institute of Physics, Maria Curie-Skłodowska University,
20-031 Lublin, pl. M. Curie-Skłodowskiej 1, Poland

JÓZEF DĄBEK, LESZEK MICHALAK, ANDRZEJ PELC

The source of gaseous clusters for mass-spectrometric investigations

Źródło klasterów gazowych do badań masowo-spektrometrycznych

1. INTRODUCTION

The cluster production by the adiabatic gas expansion method has been known since 1956 and is today the most commonly used technique to produce neutral gaseous clusters. In this technique a gas expands from a high-pressure gas chamber (typically from several Torr up to several kTorr) through a small orifice (nozzle) (typically diameters: from several up to several hundreds μm) into an evacuated region $p < 10^{-3}$ Torr. The temperature of gas in a gas chamber is usually changed from the room to the liquid nitrogen temperature. The application of high stagnation gas pressure and a small orifice causes that it is a supersonic gas flow. The collisions of particles during the hydrodynamic expansion give rise to unique properties of a supersonic beam, i.e. cooling of the rotational, vibrational and translational degrees of freedom and condensation via supersaturation. The amount of condensation (size of neutral clusters) results from the used gas stagnation pressure and its temperature, the diameter and shape of expansion nozzle. It results from many experiments [1–4] that both cluster size (number of atoms per cluster) and cluster-beam mass flux density increase with increasing source pressure p_0 and decreasing source temperature T_0. Gases with a high boiling temperature and a high ratio of specific heats $\gamma = c_p/c_v$, are more efficient for producing cluster beams [5–7].

The molecular beam containing clusters is introduced through a skimmer into an ion source where it is crossed with any ionizing agent (electrons, photons, atoms, ions) of sufficient energy and intensity. The cluster ions produced may

be analysed immediately or after additional experiments with a mass spectrometer. Although different detection techniques have been used the basis set-up of the so-called molecular beam ionization mass spectrometers (e.g. either time-of--flight, quadrupole or sector fields) are quite similar.

2. EXPERIMENTAL

In our laboratory we used mass-spectrometric technique for investigations of gaseous clusters. Figure 1 shows the detailed view of the cluster beam production, the electron ionization source and the ion extraction optics of the double--focusing sector field mass spectrometer MX1321.

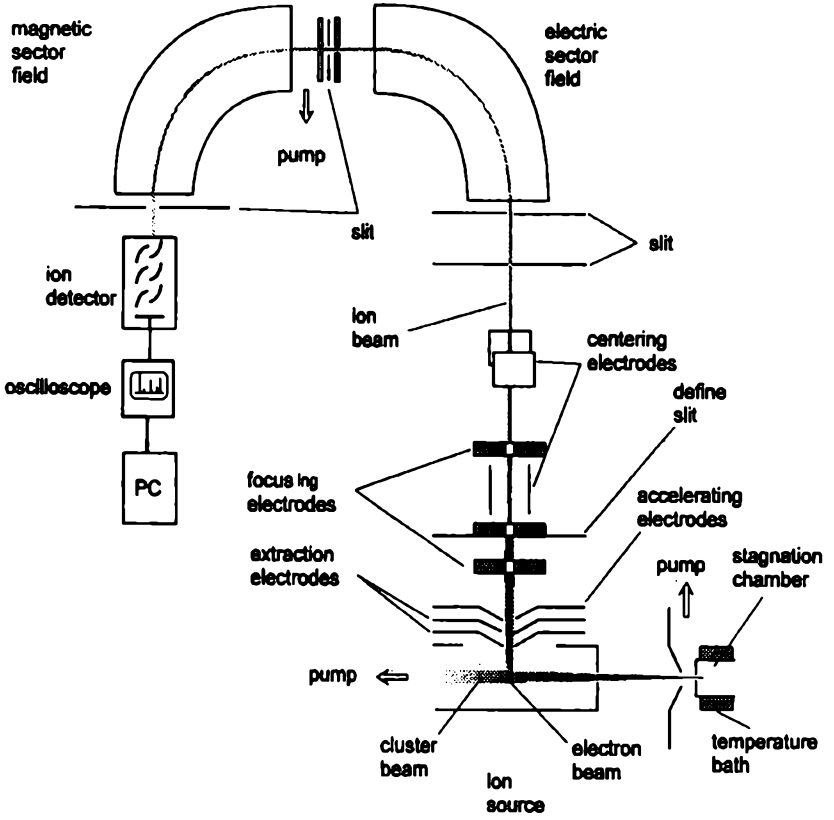

Fig. 1. The detailed view of the cluster beam production, the electron ionization source and the ion extraction optics of the double-focusing sector field mass spectrometer MX1321
Schemat wytwarzania wiązki klasterów, źródła jonów i optyki jonowej podwójnie ogniskujacego spektrometru mas MX 1321

The molecular beam (containing clusters) is introduced to the ion source where it is ionized by electrons. The energy of electrons can be changed in range 0–90 eV at the intensity of the electron beam of 0–40 μA. The potential of the collision chamber of ion source with respect to the grounded exit slit electrodes is +4kV. The cluster ions produced are formed into the ion cluster beam by the system of focusing electrodes. Before the entrance to the electric sector field the cluster ion beam is centred by a two (x,y) centering electrodes and then focused and mass analysed by the electric and magnetic (90°) sector fields. The cluster ions with the defined ratio m/z (m, z — are mass and charge of ion, respectively) are introduced via the ion detector slit to the electron multiplier. The spectrum of cluster ions can be observed on the oscilloscope and recorded by the computer.

The vacuum system of the presented apparatus is of a differential type and independently evaluates the ion source-sector fields-ion detector regions (pumping speed $700ls^{-1}$) and the cluster source region (the pumping system speed $800ls^{-1}$). The double focusing sector field mass spectrometer is able to perform ion analyses in the mass range 1–1000 u.

Figure 2 shows the detailed view of a sample (gas or liquid) dosing system used in the presented investigations. The pressure of the investigated sample is controlled by the Compact Piezo Gauge APR 262–Balzers, and temperature by the thermocouple.

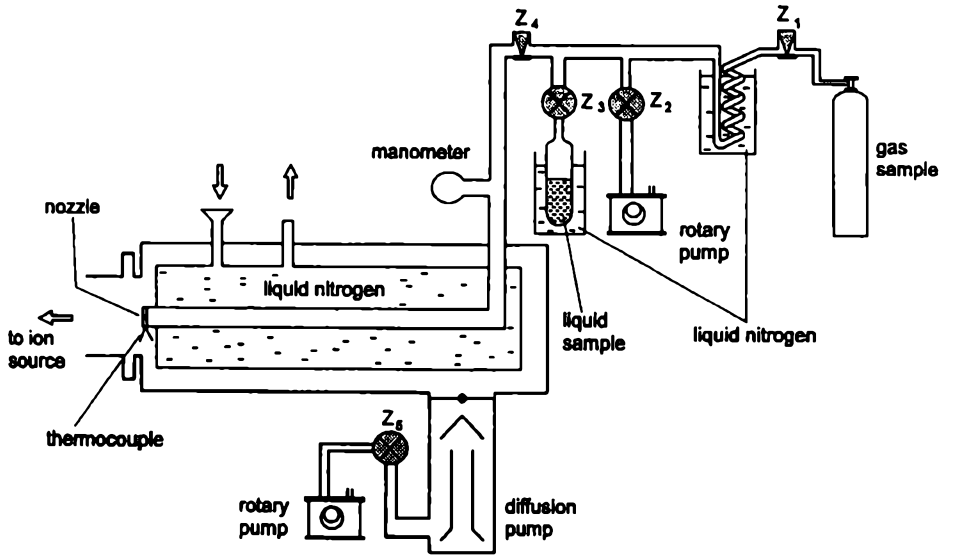

Fig. 2. The gas or liquid dosing system used in presented investigations
Układ dozujący próbki gazowe i ciekłe, używany w prezentowanych badaniach

For the testing of the cluster production we used two versions of the cluster source-beam introducing system. In version I (Fig. 3) a cluster beam is formed directly by the nozzle (40μm nozzle diameter) placed in the distance 7mm from the electron beam of the ion source. The nozzle is connected with the gas stagnation chamber via the cooper tube with the inner diameter of 3mm. The real temperature of the nozzle is a little higher than the measured temperature at the end of the gas stagnation chamber (gradient temperature along the cooper tube). In this configuration of the cluster source, the ion source and the vacuum system the maximum pressure in the gas stagnation chamber is about 300Torr. For the higher pressure of a gas sample the vacuum in the ion source region deteriorates very much. The advantage of this version is a good transmission of produced cluster between the cluster source and the ion source (relatively a short distance between the nozzle and the ion source).

In version II (Fig. 3) by using a skimmer and the differential pumping system the gas pressure in the gas stagnation chamber can be increased up to 1.5kTorr. In this version the temperature of expanded gas is controlled by the thermocouple placed just at the nozzle.

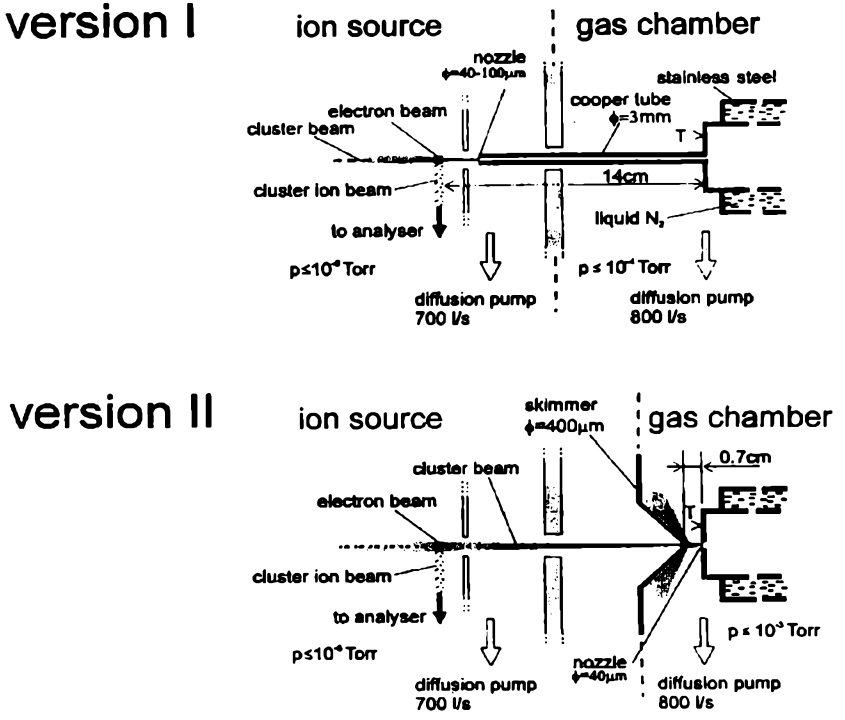

Fig. 3. The two versions of the cluster source-beam introducing system
Dwie wersje układu formowania i wprowadzania wiązki klasterów

3. RESULTS

The results of mass-spectrometric investigations of gaseous clusters are presented in Figures 4–7. The results for an air sample were obtained in version I of the cluster source and results for argon in version II (Fig. 3). Figure 4a shows the mass spectra of air clusters produced by supersonic expansion (100μm nozzle diameter) under two different experimental conditions: gas stagnation pressure p = 20 Torr and stagnation temperature T = 298K; p = 300Torr and T = 120K. The electron energy was 80eV and the intensity of the electron current was 30μA. Figure 4*b* shows the part of the spectrum from Figure 4*a* with marked different configurations of ion clusters. Figure 5 shows the ion current intensity of observed air clusters ((*a*) $(N_2)^+_{x=1-17}$; (*b*) $(O_2)^+_{y=1-15}$; (*c*) $(O_2)(N_2)^+_{x=1-15}$; (*d*) $(N_2)(O_2)^+_{y=1-12}$) versus the *m/z* ratio (size of single charged ion clusters).

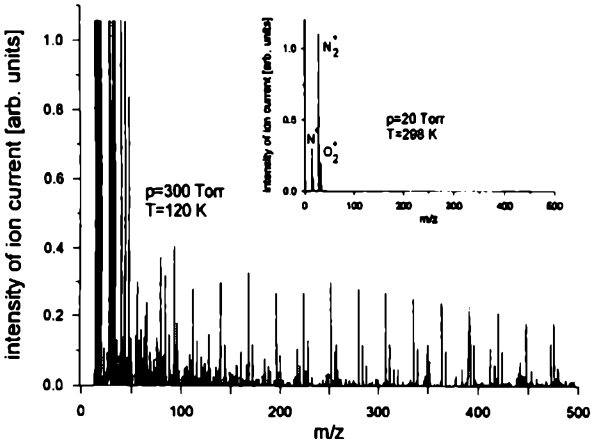

Fig. 4*a*. The mass spectra of air clusters produced by supersonic expansion (100μm nozzle diameter) under two different experimental conditions: stagnation pressure p = 20Torr and stagnation temperature T = 298K; p = 300Torr and T = 120K. The electron energy was 80eV and the intensity of the electron current 30μA

Spektrum masowe otrzymane podczas adiabatycznego rozprężania próbki powietrza (100μm — średnica dyszy), gdy ciśnienie gazu p =20Torr i temperatura gazu T = 298K; p = 300Torr i T = 120K. Energia elektronów wynosiła 80eV, a natężenie prądu elektronowego 30μA

Figure 6 shows a mass spectrum of argon clusters produced by supersonic expansion of argon for: stagnation pressure p = 370Torr; nitrogen stagnation temperature; electron energy 80eV and the intensity of the electron current 40μA. The intensity of the ion current as a function cluster size shows an exponential dependence, approximately. For example, Figure 7 shows the ion current intensity of the ion cluster Ar^+_3 as a function of the argon stagnation pressure at the liquid nitrogen stagnation temperature.

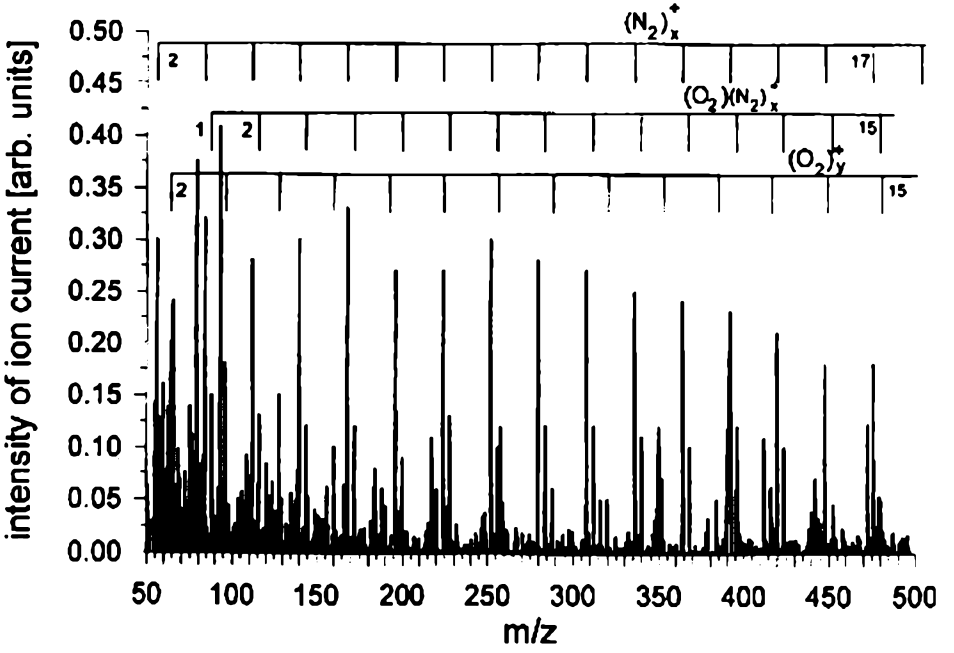

Fig. 4*b*. The part of the spectrum from Figure 4a. Observed ion clusters: $(N_2)^+_{x=1-17}$; $(O_2)^+_{y=1-15}$; $(O_2)(N_2)^+_{x=1-15}$; $(N_2)(O_2)^+_{y=1-12}$

Część widma z ryciny 4*a*. Obserwowane jony klasterów: $(N_2)^+_{x=1-17}$; $(O_2)^+_{y=1-15}$; $(O_2)(N_2)^+_{x=1-15}$; $(N_2)(O_2)^+_{y=1-12}$.

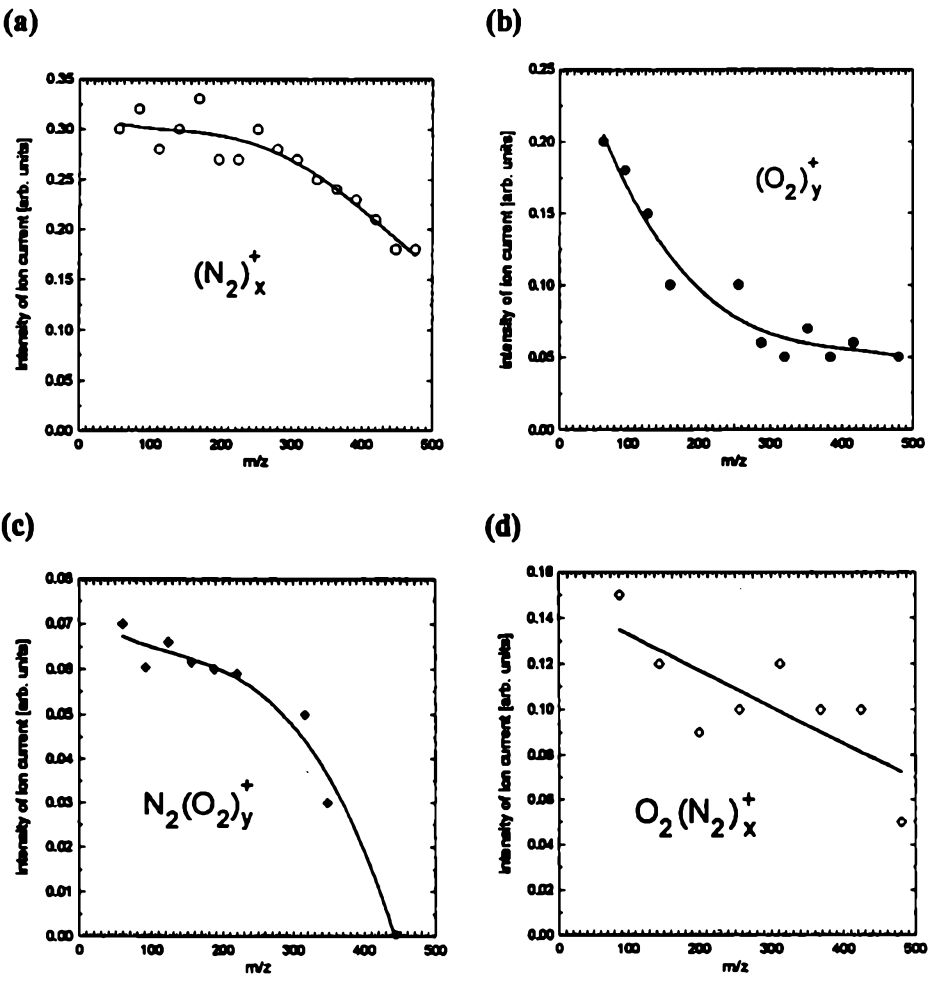

Fig. 5. The intensity of ion current for observed air clusters versus the *m/z* ratio (size of single charged ion clusters): (*a*) $(N_2)^+_{x=1-17}$; (*b*) $(O_2)^+_{y=1-15}$; (c) $(O_2)(N_2)^+_{x=1-15}$; (*d*) $(N_2)(O_2)^+_{y=1-12}$
Natężenie prądu jonowego obserwowanych klasterów powietrza w funkcji stosunku *m/z* (rozmiar pojedynczo naładowanych jonów klasterów): (*a*) $(N_2)^+_{x=1-17}$; (*b*) $(O_2)^+_{y=1-15}$; (*c*) $(O_2)(N_2)^+_{x=1-15}$; (*d*) $(N_2)(O_2)^+_{y=1-12}$

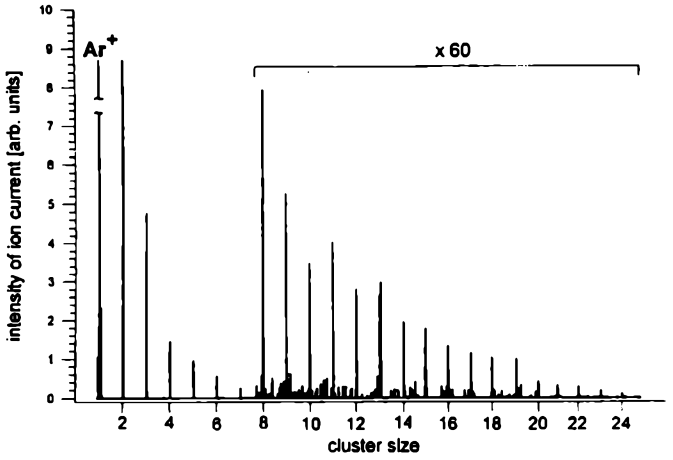

Fig. 6. The mass spectrum of argon clusters produced by supersonic expansion for: stagnation pressure p = 370Torr; nitrogen stagnation temperature; electron energy 80eV; the intensity of the electron current 40μA

Widma masowe klasterów argonu produkowanych podczas wypływu naddźwiękowego, przy ciśnieniu p = 370Torr i temperaturze ciekłego azotu, energii elektronów 80eV, natężeniu prądu elektronowego 40μA

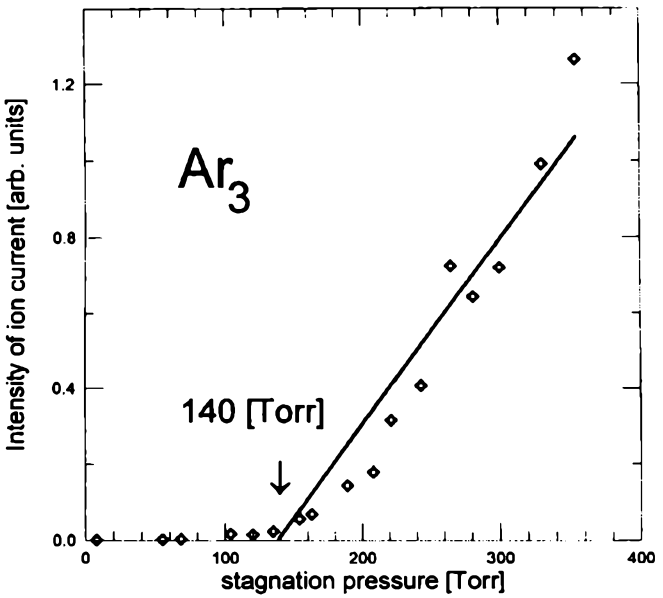

Fig. 7. The intensity of the ion current Ar^+_3 as a function of an argon stagnation pressure at the established, liquid nitrogen stagnation temperature

Natężenie prądu jonowego Ar^+_3 w funkcji ciśnienia argonu przy ustalonej temperaturze (temperatura ciekłego azotu)

4. CONCLUSION

The production of gaseous clusters by gas expansion and using a skimmer and the differential pumping system (version II) is much more useful than the system introducing an expanded beam without a skimmer. A spectra of ion clusters obtained without a skimmer are more complicated and more difficult for analyse than spectra obtained with a skimmer system. It probably results from the presence of non-condensed gas and clusters in the ion source region. In this case the ion molecule reactions and ion fragmentation processes can play a very important role.

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STRESZCZENIE

W artykule przedstawiono rezultaty masowo-spektrometrycznych (przy użyciu podwójnie ogniskującego spektrometru mas) badań produkcji klasterów gazowych otrzymywanych podczas adiabatycznego (naddźwiękowego) rozprężania próbek powietrza i argonu. Przetestowano dwie wersje źródła klasterów, różniące się zastosowaniem diafragmy separującej, umieszczonej pomiędzy dyszą formującą wiązkę klasterów a źródłem jonów spektrometru mas.