

# Mechanism of Fragmentation and Atomization of Molecular Ions in Gasdynamic Transport Cell

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**Abstract**—The fragmentation of molecular ions formed upon the electro spraying of a sample and transported through the gasdynamic system of a mass spectrometer equipped with an IESAP (Ion Extraction from Solution at Atmospheric Pressure) source has been experimentally studied. It is established that ion fragmentation in a Kantorowicz–Gray type cell takes place in the immediate vicinity of a skimmer port, apparently, as a result of collisions between ions (accelerated in an electric field) and stagnant gas. Molecular mechanisms of fragmentation are considered and it is concluded that this process can take place in a single ion–molecule collision event.

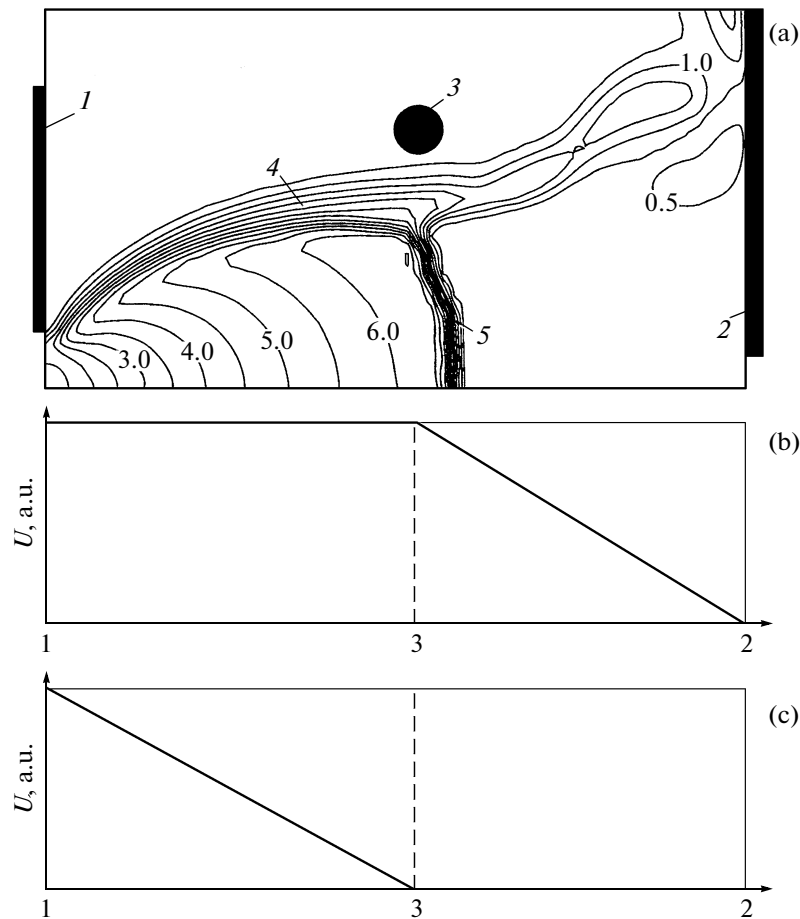
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Modern mass spectrometry widely employs the ionization technique based on electro spraying liquid samples at atmospheric pressure followed by ion extraction to high vacuum via a gasdynamic transport cell (electrospray ionization, ESI), which is an important approach to studying heavy organic biomolecules. American scientist John B. Fenn was awarded the Nobel Prize in chemistry in 2002 for his investigations in this field [1]. The phenomenon of electro spraying was originally used for the mass-spectrometric analysis of ions of both organic and inorganic molecules at the Institute for Analytical Instrument Making (St. Petersburg) [2], where this method was referred to as the ion extraction from solutions at atmospheric pressure (IESAP). A difference of the IESAP from the classical ESI method consists in that the use of a gasdynamic cell (ensuring the transport of ions from the region of atmospheric pressure to high vacuum) in IESAP is combined with the possibility of controlled fragmentation and even atomization of molecular ions. This circumstance allows the IESAP to be applied not only to the molecular, but to the elemental and isotope analysis as well. In the literature, the term IESAP refers specifically to the aforementioned ESI modification including the controlled fragmentation of ions directly in the source [3].

A gasdynamic transport cell for the IESAP in the classical variant represents a system of the Kantorowicz–Gray type (Fig. 1a) with a coaxial arrangement of

the nozzle (1) and skimmer (2). In our experiments, the input nozzle diameter was 0.5 mm, the skimmer hole diameter was 0.1 mm, the nozzle–skimmer distance was 5–7 mm, and the pressure in the cell was ~10 Torr [3]. The skimmer design can vary; in particular, we used a flat skimmer model comprising a plate with a hole analogous to the nozzle, which ensures a simple structure of the transporting electric field. A voltage pulling ions through the cell, which is applied between the nozzle and skimmer, amounts to 30–50 V for the cell operating in the molecular regime and reaches 600–800 V in the regime of atomization of strong ions such as those of rare-earth metals and actinides [3].

The residual pressure in the cell is on the order of  $10^{-2}$  of the atmospheric pressure. Owing to this drop, the gas jet passing through the nozzle is accelerated to a supersonic velocity and acquires a characteristic shock-wave structure with a compression shock and a Mach barrel. Figure 1a shows the lines of equal Mach numbers (iso-Mach contours) for a gas flow calculated by the Godunov method in the axisymmetric approximation using a program written by one of the authors (S.V.B.) [4]. This program was repeatedly tested by comparing the results of numerical calculations for model systems to the corresponding analytical solutions and experimentally measured distributions of gas velocities. It was confirmed that the program ensured



**Fig. 1.** Schematic diagram of a gasdynamic transport cell for the IESAP and the structure of physical fields in this system: (a) iso-Mach contours and the arrangement of walls and electrodes, including (1) nozzle, (2) skimmer, (3) electrode, (4) Mach barrel, and (5) compression shock (figures at the contours indicate the corresponding Mach numbers); (b) potential profile along the line connecting the nozzle and skimmer centers for equal potentials of the nozzle and electrode; (c) potential profile along the line connecting the nozzle and skimmer centers for equal potentials of the electrode and skimmer.

the calculation of gasdynamic fields with high precision and reliability [5].

The motion of ions in the cell proceeds under the combined action of gasdynamic flows and electric fields [6, 7]. All practically important cases obey conditions of the so-called electrogasdynamic approximation, according to which (i) the energy of the charged gas fraction is very small compared to the gasdynamic energy and (ii) the motion of ions does not disturb the gas flows. It should be noted that, the present-day state of the art cannot provide full correct description of the motion of ions in a gas flow and does not allow the process to be simulated, since the existing notions concerning ion mobility fail to be valid in the region of supersonic flows and compression jumps, while formalisms developed, e.g., in [7] are insufficiently strict. Therefore, we have to restrict the consideration to estimations obtained using simplified models. In particular, in the zero-field case, ions move with the gas flow; in contrast, in a dense stagnant gas with

applied field, ions will move along the trajectories that are close to the field lines [7].

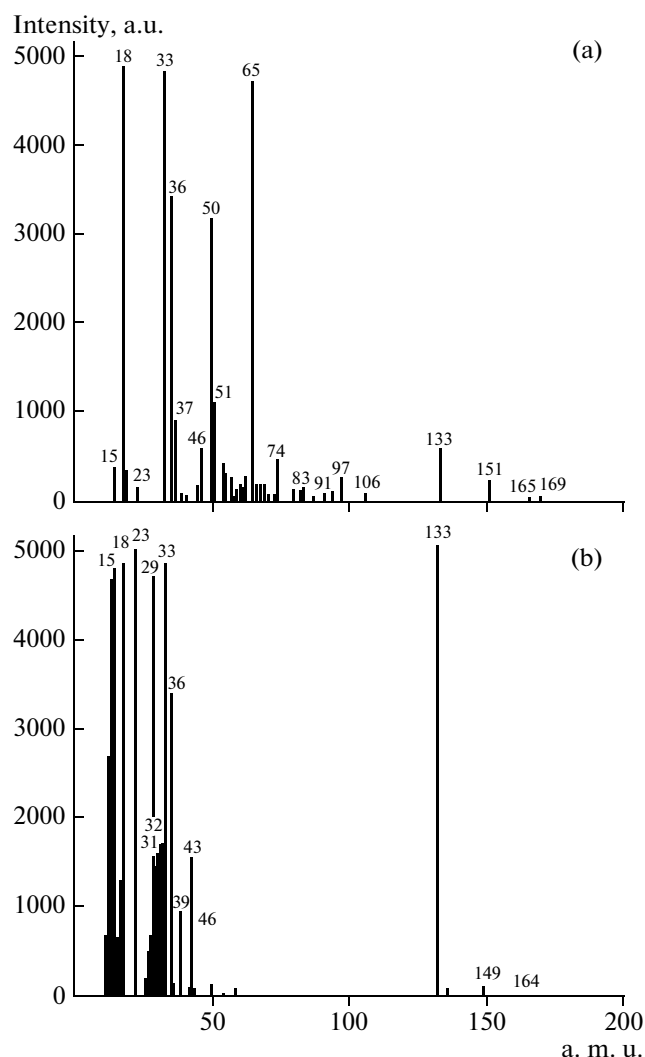
Despite extensive investigations and active discussions [8, 9], the molecular mechanism of fragmentation in the IESAP still remains unclear. In particular, it is not known in what part of the cell molecular ions exhibit decay. Earlier [8], it was suggested that the most important processes take place when ions accelerated by the applied field and moving at supersonic velocities inside the Mach barrel collide with almost stagnant gas in the region of the compression shock (4 in Fig. 1a). According to another possible variant, ions decay in collisions with gas species upon the acceleration in strong electric fields arising near the skimmer.

In order to experimentally verify both these assumptions, we have modified the cell by arranging an additional (intermediate) ring electrode immediately behind the compression shock. The modified cell was mounted on a static MX-3303 mass spectrometer

with double focusing, which is described elsewhere [6]. The additional electrode was made of a thin wire (with a diameter of 0.5 mm) and almost did not introduce perturbations in the flow. At the same time, this electrode significantly modified the potential distribution in the cell, in particular, it allowed electric fields in the Mach barrel and near the skimmer to be independently controlled. Indeed, by applying various voltages to this electrode, the electric field could be changed in the regions both in front of the compression shock and behind it. In particular, it was possible to ensure an almost zero-field regime in space in the region of the Mach barrel (Fig. 1b) or near the skimmer (Fig. 1c). In the latter case, the sensitivity of the instrument substantially dropped, but the signal was still sufficient for measuring mass spectra. Figures 1b and 1c qualitatively illustrate potential distributions in the flat capacitor approximation and with neglect of the space charge, respectively.

Figure 2a presents a mass spectrum measured in the absence of fragmentation, which was obtained during electrospraying of a model solution of cesium nitrate ( $10^{-4}$  M) in 90% methanol + 10%  $H_2O$  mixture. This spectrum was measured using a modified cell at a small potential difference ( $\sim 5$  V) between the additional electrode and skimmer. The spectrum displays, besides the peak of atomic  $Cs^+$  ion ( $m/z = 133$ ), well pronounced molecular ion peaks due to hydrated and oxidized cesium including  $CsH_2O^+$  ( $m/z = 151$ ),  $CsO_2^+$  ( $m/z = 165$ ),  $Cs-(H_2O)_2^+$  ( $m/z = 169$ ), and some other. In addition, there is an intense “chemical noise” (for  $m/z$  ranging from 16 to  $\sim 80$ ) related to the presence of impurities in the solvent and residual atmosphere. The structure of this spectrum and the relative intensities of peaks were virtually independent of the voltage in a range of 0–350 V (above which the gas breakdown took place) applied between the nozzle and intermediate electrode (i.e., in the Mach barrel region). Note that a fully analogous mass spectrum was observed with a nonmodified cell (deprived of the intermediate electrode) at low voltages applied between the nozzle and skimmer.

The mass spectrum exhibited dramatic changes when the voltages applied between the intermediate electrode and skimmer was increased to 250–300 V (Fig. 2b). In this case, the mass spectrum displayed virtually no peaks of molecular ions containing cesium, so that the only signal the given region was the intense peak with  $m/z = 133$ , which corresponded to  $Cs^+$  ion. The region of chemical noise significantly narrowed and these peaks were only observed for  $m/z = 16-19$ ,  $24-34$ , and  $42-46$ , which corresponded to the solvent and atmospheric gases. Analogous spectra were obtained using the cell without addi-



**Fig. 2.** Mass spectra of a model solution measured on an MX-3303 spectrometer equipped with a modified IESAP cell containing the intermediate electrode: (a) for a voltage of 160 V applied between the nozzle and additional electrode and 60 V between the electrode and skimmer; (b) for a voltage of 160 V applied between the nozzle and additional electrode and 160 V between the electrode and skimmer.

tional electrode, at a voltage of 450–500 V applied between the nozzle and skimmer.

Thus, the experiments showed that the fragmentation of molecular ions is absent in the Mach barrel and takes place in the region between the compression shock and skimmer.

Let us analyze the obtained results. The molecular ions exhibit fragmentation as a result of collisions with gas molecules, which can proceed according to various possible mechanisms. The simplest mechanism assumes that the energy of a single collision is comparable with that of intramolecular bonds and, thus, a molecule decays into fragments already upon a single

collision. Let us evaluate the probability of this channel. The average energy  $E_{Av}$  gained by an ion between collisions can be estimated as follows:

$$E_{Av} = eE\lambda,$$

where  $e$  is the ion charge,  $E$  is the electric field, and  $\lambda$  is the mean free path between collisions. At a residual gas pressure of  $\sim 10$  Torr, we have  $\lambda \sim 10^{-6}$  m. The electric field at an interelectrode distance of 1–2 mm and the aforementioned applied voltages amounts to  $E \sim 10^3$  V/cm. In this case, the average energy gained by a singly-charged ion between collisions does not exceed  $E_{Av} \sim 0.1$  eV and, hence, is insufficient for the fragmentation since the intramolecular bond energies are on the order of 1–2 eV [10]. Therefore, the fragmentation can only take place as a result of energy accumulation and distribution between valence bonds of a molecule [11]. The mechanism described above generally coincides with commonly accepted notions for low-pressure collision cells [12], although there are distinctive features in details.

It should be noted that, in the case of a cone-shaped skimmer, the electric field is concentrated in the immediate vicinity of its vertex and can reach a level of  $10^4$  V/cm and above, which makes fragmentation in a single collision possible. Note also that the ion mean free path in a gas is not clearly determined and exhibits a certain distribution analogous to the Maxwell distribution of particle velocities [13]. On the wings of this distribution function, very significant energies can be accumulated even for single collisions in fields on the order of  $10^3$  V/cm. Indeed, every 5000th collision at room temperature involves an energy that is ten times the average value and, hence, is sufficient for fragmentation in the case under consideration. On traveling a distance from the compression shock to skimmer ( $d \sim 2$  mm) at a residual pressure on the order of 10 Torr, each ion experiences on the average 2–3 thousand collisions, which is close to the aforementioned value [13]. It is also interesting to note that more strongly bound ions such as water and molecular fragments of methanol (belonging to the chemical noise) are not susceptible to atomization. The mechanism of this phenomenon is still not completely clear, but it can be suggested that, due to the significant binding energy ( $\sim 4$ – $5$  eV), the probability of decay for these molecules is very small.

In conclusion, our experimental data unambiguously indicate that the fragmentation of molecular ions takes place near the skimmer rather than in region of supersonic gas flows. The estimations show that this fragmentation can actually take place as a result of collisions between ions accelerated by an electric field and molecules of the gas phase.

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