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The smoke ion source: a device for the generation of cluster ions via inert gas condensation

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We report the development of an ion source for generating intense, continuous beams of both positive and negative cluster ions. This device is the result of the marriage of the inert gas condensation method with techniques for injecting electrons directly into expanding jets. In the preliminary studies described here, we have observed cluster ion size distributions ranging from $n=1$–400 for Pb_n^+ and Pb_n^-, and from $n=12$–5700 for Li_n^-.

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Introduction

In both science and high technology there is a need for high intensity sources of large cluster ions comprised of relatively high temperature materials. In recent years, both spectroscopic and kinetic studies of cluster ions have begun to explore the world of aggregated phenomena lying in the size regime between single atoms and molecules and the solid state [1, 2]. At the same time, interest has continued to grow in the potential applications of cluster ions to thin film formation, size-specific catalyst preparation, ion beam sputtering, and ion lithography [3, 4].

Here, we report the development of a source for generating intense, continuous beams of large cluster ions made up of lead or lithium atoms. This device is the result of combining the inert gas condensation method with techniques for injecting electrons directly into expanding jets. Inert gas condensation is a proven approach for generating strong beams of large neutral clusters comprised of relatively high temperature materials [5–10]. In inert gas condensation cells an oven evaporates the material of interest into a bath of cool inert gas. In this environment the evaporated material condenses to form a dilute smoke composed of ultra-small particles and clusters. An orifice allows the inert gas, along with its entrained smoke, to exit the cell into a high vacuum region where a beam is formed. The injection of low energy electrons directly into the high density portion of supersonic expansions has been shown over the past few years to be a highly efficient method for generating both positive and negative cluster ions [11–13]. The electrons can be provided either by an electron gun or by a biased hot filament. In the past, usually in the course of mass spectrometric characterization of their inert gas condensation sources, several investigators have generated positive cluster ions from inert gas condensation cells by subjecting the neutral cluster beams to electron bombardment or laser ionization well downstream of their cells' exit apertures [7–10, 14, 15]. In the present work, electrons from a biased filament are injected, in a close-coupled manner, directly into the weak jet expansion of smoke-containing inert gas as it leaves the condensation cell to generate intense beams of large positive and negative cluster ions composed of lead or lithium. We refer to the unique union of these two techniques as the Smoke Ion Source. We anticipate that large cluster ions of much higher temperature materials can also be generated with this source. Below, we describe the smoke ion source and its associated apparatus along with our preliminary experiments with the test materials, lead and lithium.

Experimental

A schematic diagram of the Smoke Ion Source is presented in Fig. 1. The material of interest is evaporated from a heat shielded oven (O) by direct resistive heating. The oven assembly is separated from the inert gas condensation cell (CC) by a water cooled copper box (CB) which serves to thermally isolate the cool inert gas environment from the high temperature region. Vapor effusing from the oven then enters the cool inert gas environment. The condensation cell typically contains from 0.5 to 10 torr of helium which can be maintained at constant temperatures between 77 K and 285 K by a coolant reservoir (CR). The cool inert gas thermally quenches the vapor causing supersaturation with subsequent condensation and cluster growth. The condensation cell is coupled to high vacuum by a small (1.0–1.5 mm diameter) aperture (A). The flow of the helium entrains the clusters and transports them into the high vacuum region via a weak jet expansion. The smoke flux is rather high and reasonably directional as evidenced by the rapid formation of opaque deposits on glass targets placed about 1 cm in front of the aperture.

Electrons are injected into the smoke-containing helium flow by a negatively biased hot filament (I) immediately as it leaves the aperture. Axial magnetic fields in this region were found to greatly enhance cluster ion production. The entire source is biased at either ±500 V or ±1 kV with respect to ground potential. The generation of both positive and negative cluster ions utilizes the same electron injection configuration. When switching from negative to positive ions, necessary voltage changes involve reversing appropriate electrode polarities and using a higher filament bias voltage.

The resulting beam of cluster ions and accompanying neutrals is skimmed before entering the rest of the apparatus. Briefly, this apparatus consists of an ion optical beam line, an **E** × **B** mass separator (Wien filter), and a Faraday cup for ion detection. The Wien filter can be operated at a high electrostatic field where it achieves normal mass resolution over a limited mass range, or at a low electrostatic field where it exhibits poor resolution but over a much larger mass range. The latter condition is especially useful for detecting very large cluster ions. At Wien filter electrostatic fields of a few volts and with a beam voltage of 1 kV, our available mass range extends up to 80,000 amu. Also, given the high ion currents observed, we can use a Faraday cup for ion detection. Since Faraday cups measure only impinging charges, they are able to detect both high and low mass ions with equal effici-

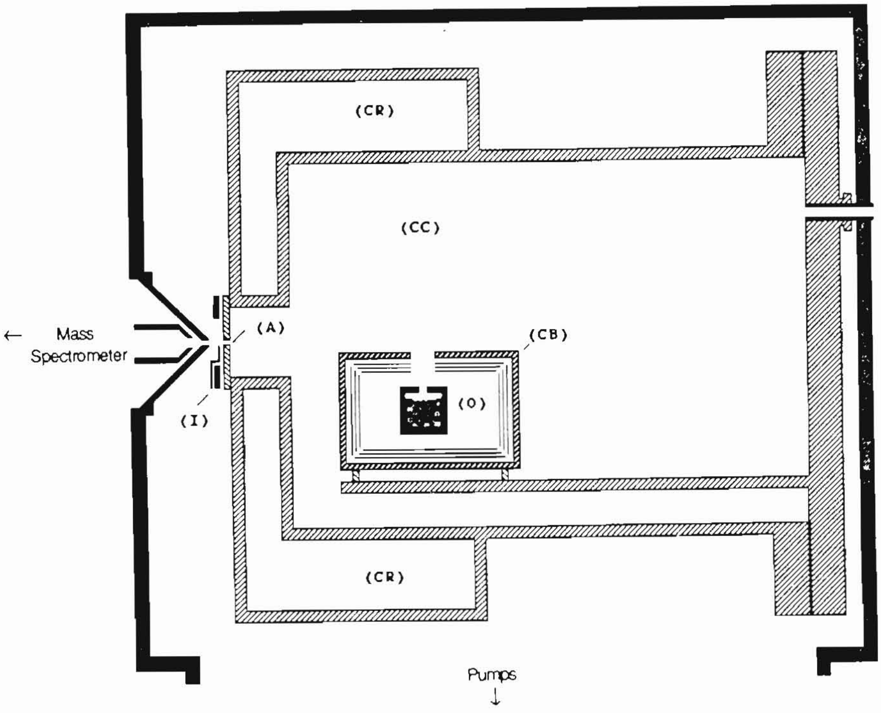

Fig. 1. Schematic diagram of the Smoke Ion Source

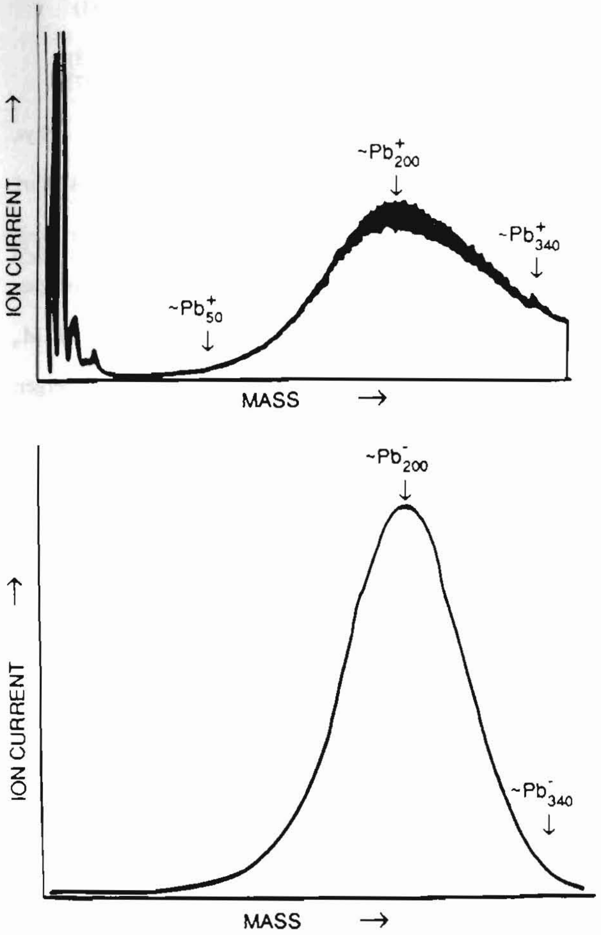

Fig. 2. Mass spectra of large positive and negative cluster ions of lead generated using the Smoke Ion Source

ency, bypassing the difficulties associated with detecting large cluster ions with particle multipliers.

Source performance: generation of cluster ions

Here, we describe the results of our preliminary experiments with the test materials, lead and lithium. Lead cluster ions were generated under two different sets of source conditions. The first set utilized a source aperture diameter of 1.0 mm, a helium pressure of 6.0 torr maintained at 195 K, and an oven temperature of 1460 K. Figure 2 presents mass spectra for both positive and negative lead cluster ions recorded under these conditions. In order to obtain these spectra, the Wien filter was operated in its high mass range mode. Both spectra exhibit a progression of unresolved cluster ion peaks ranging from approximately 40 to 400 atoms per cluster ion. For both polarities, the maximum in the size distribution corresponds to about 200 atoms per cluster ion. In the anion spectrum, an ion current of 600 pA was observed at this maximum. If average currents of cluster anions are compared, this is about five orders of magnitude more intense than those available via laser vaporization techniques [16]. In the cation spectrum, we observe a series of low mass peaks due to Pb^{++} and $Pb^+_{n=1-3}$ in addition to its high mass distribution. Interestingly, these low mass peaks are absent in the anion spectrum. This difference suggests that the small lead cluster cations may result from fragmentation. The rough similarity between the high mass distributions of these spectra, on the other hand, may indicate that they reflect the neutral cluster distribution.

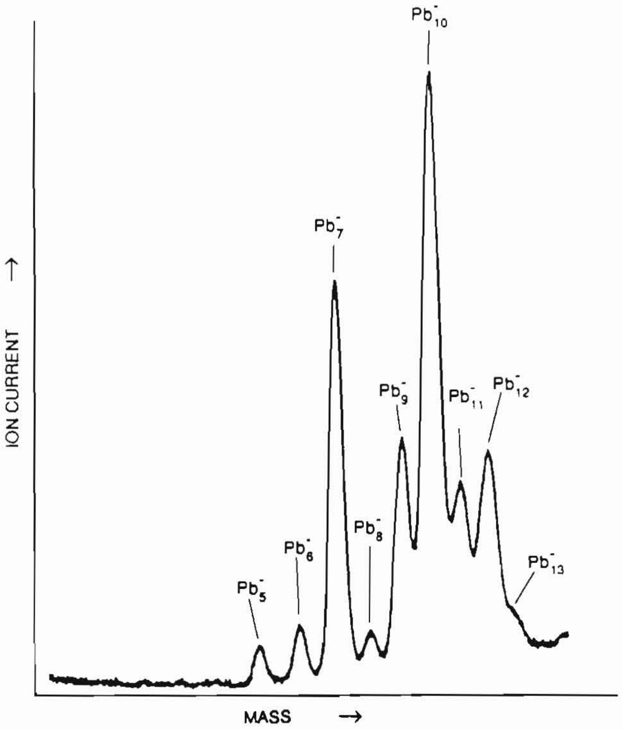

Fig. 3. Mass spectrum of small lead cluster anions generated using the Smoke Ion Source

In an effort to explore the source's ability to generate smaller cluster ions, a second set of source conditions was selected. This set utilized a source aperture diameter of 1.5 mm, a helium pressure of 1.6 torr at 273 K, and an oven temperature of 1460 K. Figure 3 shows the resultant lead cluster anion mass spectrum with the Wien filter operating in its low mass range mode. A variety of small lead cluster anions were observed demonstrating the feasibility of shifting the cluster ion size distribution by manipulating source conditions. We note that the low mass size distribution of our lead cluster anion spectra is reminiscent of Sattler's lead cluster cation distribution [8].

Experiments with lithium were performed using a 1.5 mm diameter source aperture, 1.0 torr of He at 273 K, and an oven temperature of 1150 K. This set of source conditions produced a lithium cluster anion distribution that ranged from 12 to 5700 atoms per cluster anion. In addition, we have observed total anion currents as high as 45 nA for this system.

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