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Electronic-shell-structure effects in $Cs_n{}^+$

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Relative mass abundances of singly charged cesium-cluster ions ($Cs_n{}^+$) extracted from a liquid-metal ion source show sharp decremental steps at $n = 3$, 5, 9, and 21 and a pronounced minimum at $Cs_{10}{}^+$. In the region of $n > 9$, $Cs_{13}{}^+$ shows a maximum in the relative abundance. The time-of-flight technique is used to obtain the mass spectrum. The prominent features observed at $n = 9$ and 21 are interpreted using the shell structure of simple metal clusters. $Cs_9{}^+$ and $Cs_{21}{}^+$, which contain 8 and 20 valence electrons, respectively, form closed-shell configurations with enhanced relative stabilities.

INTRODUCTION

Small metal clusters, their structure, stability, and properties, are subjects of intense interest.[1,2] The pioneering investigations of Knight *et al.*[3,4] and the development of the electronic shell structure of clusters of simple metals (particularly groups IA and IB) have simulated much activity in this area. Besides magic numbers, other properties of small, simple metal clusters, e.g., static polarizabilities, ionization potentials, and surface plasma resonances have also been successfully explained on the basis of the electronic shell structures.[5-8] Relative abundances of cluster ions of metals ($Rb_n{}^+$, $Li_n{}^+$, $Cu_n{}^+$, $Ag_n{}^+$, $Zn_n{}^+ \ldots$), extracted by widely different methods, also show pronounced features which are explained on the basis of the electronic shell structure.[9-11] In this paper we report on our experimental observations on the shell-structure effects observed in the singly charged cluster ions of cesium ($Cs_n{}^+$) extracted from a liquid-metal ion source (LMIS). In an earlier paper[10] we reported similar observations on $Rb_n{}^+$. Our principal motivation for studying heavier alkali-metal clusters is to examine the role of spin-orbit effects on the shell structure of these simple metal clusters.

EXPERIMENT

The schematic of the experimental apparatus is shown in Fig. 1. The details of the apparatus have been presented in our earlier papers.[10,12] Only a limited description of it will be presented here. We use a capillary-type LMIS for the production of $Cs_n{}^+$. About 2 g of Cs (from glass ampules) are loaded into the oven and placed inside a high vacuum chamber with residual gas pressure in the low 10^{-7}-Torr region. By differential heating, Cs is distilled into the tungsten capillary needle which is heated to keep the Cs in the liquid state (melting point ~30 °C). Copious production of ions results when the potential difference between the tungsten needle and the extractor exceeds 2 KV. The electrostatic lens assembly collimates the ion beam. The mass spectra is obtained using the time-of-flight technique. The ion beam is pulsed by applying a voltage pulse to a pair of parallel deflecting plates (A). This causes transverse deflection of the ion beam. The drift region is about 3 m long at the end of which are two continuous dynode electron multipliers (channeltron electron multipliers CEM1 and CEM2). Energy analysis of the cluster ions is done with the energy analyzer placed in front of the CEM2. The two-detector arrangement in conjunction with the energy retarder greatly extends the scope of our investigations since it permits the detection of both charged and neutral fragments. The residual gas pressure in the drift region is in the mid 10^{-8}-Torr range.

At 3 m from the source we obtain cw ion currents as large as 60 nA at an ion kinetic energy of 2 KV. A large fraction of this is made up of Cs^+. Using a Faraday cup in place of CEM2 we obtain the absolute mass fractions in the ion beam. The Faraday cup detects cluster ions of all sizes with a uniform efficiency. However, there is no

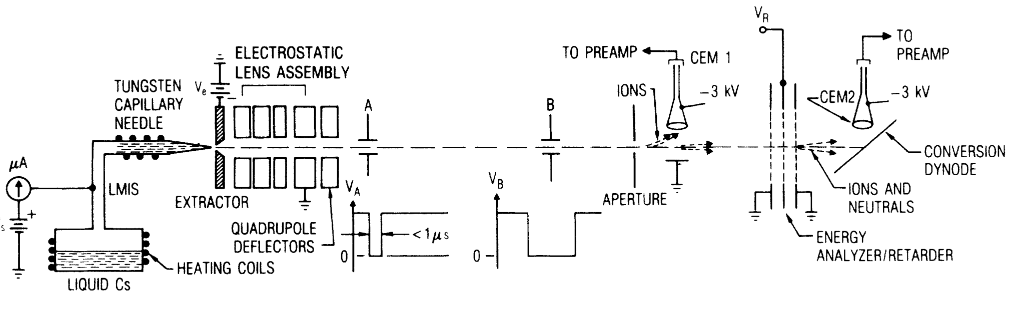

FIG. 1. Schematic of the apparatus.

gain and consequently the signal-to-noise ratio beyond Cs_5^+ is very low. Typically the relative amounts $Cs^+:Cs_2^+:Cs_3^+$ are 0.65:0.2:0.15. For low-emission currents ($<20\ \mu A$) from the ion source, clusters larger than $n=3$ constitute less than 5% of the total ion beam. For higher emission currents ($>100\ \mu A$) a very significant increase in the production of larger clusters is observed. We have studied the performance and characteristics of our ion source and have published the results.[13]

RESULTS AND DISCUSSIONS

The relative abundance spectrum of Cs_n^+ for low-emission current and for low gain of the electron multiplier is shown in Fig. 2(a). The electron multiplier directly facing the beam (CEM2) was used. The signal due to the large Cs^+ component easily saturates the electron multiplier and consequently is off scale in Fig. 2(a). There is a sharp reduction in the relative abundance of the cluster ions beyond $n=3$. In order to investigate sizes greater than 3 we block the atomic, dimer, and trimer ions from reaching the multiplier. This is done by applying a second voltage pulse to the parallel deflecting plates B. The pulse length and the delay with respect to the time-of-flight pulse (voltage pulse to A) are adjusted so that all ions smaller than Cs_3^+ are deflected off of the detector. A pulsed cluster ion beam of a single mass can be easily obtained in this arrangement. The mass spectrum of Cs_n^+ for $n\geq 4$ is shown in Fig. 2(b). The electron multiplier gain was increased by more than a factor of 30 to obtain this mass spectrum. Figures 2(a) and 2(b) are for the same low-emission current from the source. We clearly observe up to Cs_9^+ with a characteristic odd-even alternation. This type of odd-even alternation in the relative abundances has been observed in cluster ions of many metals.[9] In the singly charged cluster ions of simple monovalent metals (groups IA and IB a cluster of size n contains $(n-1)$ valence electrons. For clusters containing an odd number of atoms there is complete spin pairing of the electrons. This leads to an increase in the relative binding energy. These clusters show enhanced stability relative to the adjacent clusters containing unpaired valence electrons. There is nearly a factor of 6 reduction in relative abundance in going from $n=5$ to $n=6$. The abrupt termination of the ion signal after $n=9$ is apparent. Evidence of cluster ions larger than Cs_9^+ is shown in Fig. 2(c). However, the signal-to-noise ratio is very low in this region.

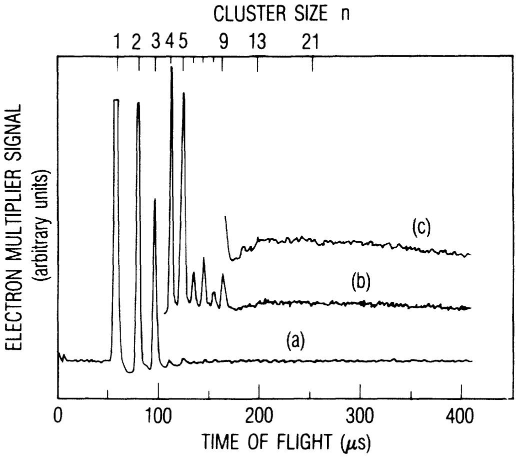

FIG. 2. Mass spectrum of Cs_n^+ obtained by the time-of-flight technique. The emission current from the tip is set to be less than 20 μA. (a) is for low-electron multiplier gain. In (b) ions smaller than and including trimers are blocked. The gain of the electron multiplier is also increased. In (c) the vertical scale is expanded to show qualitatively the presence of cluster ions greater than 9.

Larger cluster ions are generated only when the total emission current from the liquid-metal tip is increased. This is accomplished by increasing the potential difference between the tip and the extractor. Nominally, the threshold-potential difference for ion emission is ~2100 V. For a few hundred volts in excess of the threshold the characteristics of emission dramatically changes. We observe a significant current of clusters larger than Cs_9^+. This type of behavior has been observed by many investigators working with the LMIS's. Emission of multiply charged cluster ions and even-charged droplets have been reported.[14,15] The mass spectrum of Cs_n^+ obtained using CEM2, under high-emission-current conditions is shown in Fig. 3. Cluster ions smaller than Cs_6^+ were blocked to prevent overdriving the electron mutipliers. The mass spectrum shown in Fig. 3 was taken for the ion kinetic energy of 4 keV. Well-resolved mass peaks up to $n=21$ are observed. These peaks are superimposed over a broad continuous background. Energy analysis of the cluster shows that the background is primarily due to the long low-energy tails in the energy spectrum of the extracted ions. Cluster ions from the LMIS are known to exhibit large energy spreads.[16] In our experiments the energy spread severely limits the mass resolution. This background gets substantially suppressed when the energy retarder is set to a few hundred volts less than the source potential.

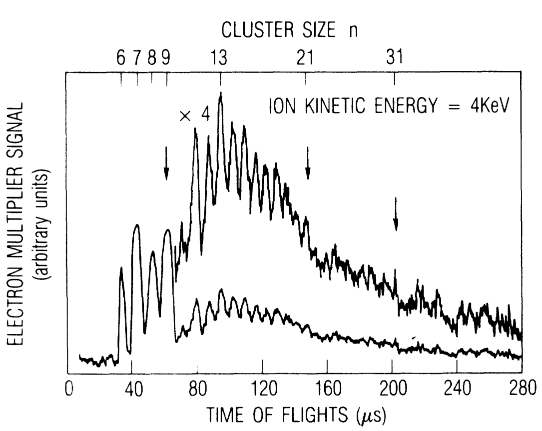

FIG. 3. Mass spectrum of Cs_{10}^+ to Cs_{21}^+. Ions smaller than Cs_6^+ are blocked. The spectrum for $n>9$ with expanded vertical scale is also shown.

The spectrum shows a rich structure in the region $9 < n < 21$. We exercise caution in comparing the amplitudes of the mass peaks due to the presence of the broad background. The flight times obtained from the peaks accurately scale as $(n)^{1/2}t_1$, where t_1 is the flight time of Cs^+. This implies that the peaks are due to the cluster ions generated from the liquid tip at the tungsten needle. However, the energy spread appears to be dependent on the size. We plan to make a careful energy analysis of various sizes and this will be published elsewhere. Preliminary studies show that there is substantial fragmentation during the flight. Another notable feature in the mass spectrum is the very low relative abundance of ${Cs_{10}}^+$. In the region of $n > 9$ ${Cs_{11}}^+$ and ${Cs_{13}}^+$ are significantly more abundant than all the rest. After ${Cs_{21}}^+$ the sudden absence of resolvable peaks is striking, although there is the sloping background beyond $n = 21$. Under very stable operating conditions of the source we have seen some evidence of cluster ions greater than 21 but the substantial improvement in the signal-to-noise ratio is required before we can draw definite conclusions. Nevertheless, the sharp edge after $n = 21$ is always reproducible. The gross features of the mass spectrum of ${Cs_n}^+$ are quite similar to those of ${Rb_n}^+$, which we have studied in considerable detail.[17] In the region of $n > 9$, the relative abundance of ${Rb_{13}}^+$ was found to be substantially larger than all the rest. Furthermore, a pronounced decremental step was observed in going from ${Rb_{19}}^+$ to ${Rb_{20}}^+$. The corresponding effect in the ${Cs_n}^+$ spectra is not as pronounced. It is quite likely that due to the large background many features are masked.

The sudden decremental steps beyond ${Cs_9}^+$ and ${Cs_{21}}^+$ can be explained on the basis of the electronic shell structure of these clusters. Saito *et al.* have observed similar effects in the relative abundance spectra of ${Li_n}^+$ and ${Na_n}^+$ extracted from a LMIS.[11] Shell-closing effects have also been observed in the cluster ions of ${Cu_n}^+$, ${Ag_n}^+$, and ${Au_n}^+$ generated by secondary-ion emission.[9] Since these cluster ions are extracted directly, without any additional photoionization process, the relative abundances of these cluster ions are directly governed by their intrinsic stabilities. For clusters with closed-shell structures the relative stability is enhanced. The spherical jellium model predicts enhanced stability for simple metal clusters containing 8, 18, 20, 34, 40, . . . valence electrons. This corresponds to closed shells $1s^21p^6$, $1s^21p^61d^{10}$, $1s^21p^61d^{10}2s^2$, $1s^21p^61d^{10}2s^21f^{14}$, $1s^11p^61d^{10}2s^21f^{14}2p^6$, . . ., respectively. The magic numbers have been observed both in neutral and charged clusters of simple metals.[3,4,9,10] ${Cs_9}^+$ and ${Cs_{21}}^+$ contain 8 and 20 valence electrons, respectively, and form closed-shell structures. This explains our experimental observations—sudden decremental steps after $n = 9$ and 21. We do not see any decremental step at ${Cs_{19}}^+$, which is predicted to be of a closed-shell configuration. We believe this is primarily due to the distorting effects of the broad background. In ${Rb_n}^+$ we observed the decremental step at $n = 19$ only after the low-energy ions are filtered off. Clusters that contain a single electron outside a closed shell (e.g., ${Cs_{10}}^+$) are low in relative abundances due to their high probability of neutral-atom evaporation to yield the energetically favorable, adjacent closed-shell configurations. Saito and Cohen have theoretically examined the evaporation probabilities of such clusters in the context of the jellium model.[18] They use the term "antimagic number" for these clusters. Their calculations show that significant monomer and dimer evaporation could occur in these clusters thereby accounting for the relatively low abundances of these clusters. The Clemenger-Nillson model,[19] which takes into account the distortion of the spherical jellium, has been used to explain the fine structures observed in the relative abundance spectra of Na_n and K_n. Our experimental data do not have enough resolution to be able to reliably examine the fine structures in the mass spectrum. To examine the spin-orbit modifications of the shell structure larger clusters would have to be examined. We are investigating ways to obtain larger clusters and also improve the mass resolution.

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