Stability of Small Neutral and Charged Strontium Clusters

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Abstract. Dissociation and fission of small neutral, singly and doubly charged strontium clusters are studied by means of ab initio density functional theory methods and high-resolution time-of-flight mass spectrometry. Magic numbers for small strontium clusters possessing enhanced stability towards monomer evaporation and fission are determined. It is shown that ionization of small strontium clusters results in the alteration of the magic numbers. Thermal promotion of the Coulombic fission for the Sr$_7^{2+}$ cluster is predicted.

PACS numbers: 31.15.Qg, 36.40.Qv, 36.40.Wa
Processes leading to the instability and the fission of metal clusters are among the most fundamental in cluster science, see e.g. [1]. Investigation of the metal clusters decay provides a direct tool for studying intrinsic stability and binding forces of these objects. Such investigations attract an increased interest, because the general features of metal clusters decay and nuclear fission are quite similar.

One can distinguish two classes of phenomena in the decay of metal clusters. The first one is dissociation or evaporation of fragments due to vibrational excitation, that makes cluster thermally metastable. The second one is fission that occurs when the repulsive Coulombic forces associated with an excess of charge overcome the electronic binding energy of the cluster [2, 3, 4, 5, 6, 7]. Multiply charged metal clusters are stable towards fission when their size exceeds the critical size of stability, which depends on the type of metal species and the cluster charge [8, 9]. In the latter case evaporation is the dominant channel of cluster decay. For the cluster sizes smaller than the critical size fission becomes more favorable [10].

The most sophisticated situation arises when the cluster size approaches the “critical size” region. It has been found experimentally that in this case the internal thermal excitation can influence fission channels and promote the Coulombic fission [11]. On the other hand fission into two charged fragments can stimulate an additional ejection of neutral atom during or immediately after the system overcomes the fission barrier. Such an interplay between the Coulombic fission and the evaporation processes has recently been observed [12].

In this Letter we report the results of theoretical and experimental investigation of stability of small neutral, singly and doubly charged strontium clusters towards the emission of neutral and singly charged fragments. We show that the closure of electronic shells of the valence electrons enhances the stability of small strontium clusters towards monomer evaporation. We demonstrate that the ionization of small strontium clusters results in the alteration of the magic numbers for strontium clusters. By ab initio molecular dynamics simulations we determine the critical appearance size for doubly charged strontium clusters as well as the region of cluster sizes in which the strong competition between evaporation and fission takes place. We predict theoretically the thermal promotion of the Coulombic fission for the $Sr_7^{2+}$ cluster and confirm the assumption made in [12] about the strong shape deformation of the fissioning $Sr_7^{2+}$ cluster.

The experimental setup is similar to that used in previous works [12, 13]. Calculations have been performed with the use of a core-polarization potential to simulate the $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ core electrons of the Sr atom. The density-functional theory based on the hybrid Becke-type three-parameter exchange functional paired with the gradient-corrected Perdew-Wang 91 correlation functional (B3PW91) has been used throughout this work (see, e.g., [14, 15] and references therein). Such an approach has proved to be a reliable tool for ab initio studies of the structure and properties of strontium clusters [16]. To find the optimized geometry of a cluster we have used the procedure described in [17, 18]. The results of cluster geometry optimization and
analysis of various isomer forms for neutral, singly and doubly charged small strontium clusters will be discussed in detail elsewhere [19]. Calculations have been carried out with the use of the GAUSSIAN 03 software package [20]. The SDD basis set of primitive Gaussians has been used to expand the cluster orbitals (see, e.g., [14] and references therein).

![B3PW91/SDD](image)

**Figure 1.** Monomer dissociation energies for neutral and singly charged Sr-clusters. Filled squares and circles: neutral monomer dissociation energies, $D_{N,1}^{0,0}$, and, $D_{N,1}^{+,0}$, for neutral and singly charged Sr-clusters, respectively. Open circles: singly charged monomer dissociation energies, $D_{N,1}^{+,+}$, for singly charged Sr-clusters. Crosses and star: experimental data.

Figure 1 shows the monomer dissociation energies for neutral and singly charged Sr-clusters as a function of the cluster size. Filled squares and circles represent neutral monomer dissociation energies, $D_{N,1}^{Z,+}$, calculated for neutral and singly charged strontium clusters respectively. Here $E_{tot}(M_N^Z)$ is the total energy of an optimized $N$-particle metal cluster with charge $Z^+$. Crosses in figure 1 show the experimental results for neutral monomer dissociation energies $D_{N,1}^{+,0}$ of singly charged strontium clusters obtained in this work. Star presents the experimental value of $D_{2,1}^{+,0}$ for the ionized strontium dimer from reference [21].

The local maxima in the size dependence of the monomer dissociation energy, $D_{N,1}^{0,0}$, at $N = 4$, 7 and 10 correspond to the most stable configurations of neutral Sr-clusters towards monomer evaporation $Sr_N \rightarrow Sr + Sr_{N-1}$. The same magic numbers have also been obtained from the analysis of binding energies of small neutral strontium [19] and magnesium [18] clusters. The electronic configuration of the strontium atom is $[Kr]5s^2$, which means that there are two valence electrons per atom. Accounting for the semi-core 4p electrons of strontium simultaneously with the valence electrons increases the absolute value of the binding energy by about 10-20% although it does not change the general qualitative trends in the properties of small strontium clusters [22].
one can state that the most stable magic clusters $Sr_4$, $Sr_7$ and $Sr_{10}$ possess $N_{el} = 8$, 14 and 20 valence electrons respectively, which is in agreement with the deformed jellium model (see, e.g., [23, 24, 25, 26] and references therein as well as discussion in [18]).

Open circles in figure 1 show the singly charged monomer dissociation energies, $D_{Z+1}^{2+,+} = E_{tot}(M_1^{(+)}) + E_{tot}(M_{N-1}^{(Z-1)+}) - E_{tot}(M_N^{Z+})$, calculated for singly charged strontium clusters. Figure 1 demonstrates that the evaporation of a charged monomer for singly charged Sr-clusters, $Sr_N^+ \rightarrow Sr^+ + Sr_{N-1}$, is strongly suppressed in comparison with the evaporation of a neutral strontium atom, $Sr_N^+ \rightarrow Sr + Sr_{N-1}^+$. The singly charged strontium dimer $Sr_2^+$ is more stable towards decay in comparison with the neutral dimer. This phenomenon has a simple physical explanation: the removed electron is taken from the antibonding orbital, and thus cationic strontium dimer is stronger bounded. The similar effect has been discussed for cationic magnesium clusters in [18].

The local maxima in the size dependence of the neutral monomer dissociation energy, $D_{N,1}^{+,0}$, for the $Sr_5^+$ and $Sr_7^+$ clusters indicate their enhanced stability towards monomer evaporation. Figure 1 clearly demonstrates that the single ionization of small strontium clusters results in the alteration of the magic numbers. The similar alteration of the magic number from $N = 4$ for neutral to $N = 5$ for cationic magnesium clusters has been noticed in our recent work [18]. This fact can be explained by the manifestation of shell effects. The singly charged alkaline earth metal clusters always possess odd number of valence electrons and, thus, always contain open electronic shells. In this case the enhanced stability of a singly charged alkaline earth metal cluster ion arises, when the electronic configuration of the ion has one hole in or an extra electron above the filled shells [18]. Thus the electronic configuration containing an extra electron becomes more favorable for $Sr_5^+$. The calculated values of $D_{N,1}^{+,0}$ are in a good qualitative agreement with the experimental results. Theoretical curve reproduces all the features in the size dependence of the dissociation energy obtained in experiment. However, the calculated monomer dissociation energies for the $Sr_4^+$, $Sr_5^+$ and $Sr_6^+$ clusters underestimate the experimental values by approximately 0.4 eV. This discrepancy can be attributed to the distribution of daughter fragments registered in experiment over different isomer states. One can assume that after evaporation of a neutral monomer the resulting daughter fragment remains not always in the ground state, but in one of the higher energy isomer states. This brings the experimentally measured dissociation energies up. This fact is not taken into account in the calculations reported. Therefore the monomer dissociation energies calculated theoretically lay lower those measured in the experiment. The results of geometry optimization of different isomer states of small strontium clusters will be discussed elsewhere [19].

Figure 2 shows the monomer dissociation energies for doubly charged $Sr$-clusters as a function of cluster size. Filled and open triangles represent the neutral and singly charged monomer dissociation energies, $D_{N,1}^{2+,0}$ and $D_{N,1}^{2+,+}$, respectively. It is important to note that the decay of doubly charged parent cluster into two singly charged daughter fragments usually involves the overcoming a fission barrier caused by the Coulombic
Figure 2. Monomer dissociation energies for doubly charged Sr-clusters. Filled and open triangles: neutral and singly charged monomer dissociation energies, $D^{2+,0}_{N,1}$ and $D^{2+,+}_{N,1}$ respectively. Filled circles: fission barriers for the process $Sr_N^{2+} \rightarrow Sr^++Sr^+_{N-1}$.

repulsion, while evaporation is the barrierless process [5, 10]. Therefore, the values $D^{2+,+}_{N,1}$ characterize the energy balance between the initial and the final states of the system and do not give direct information about the fragmentation rate, because the fission rate is usually determined by the fission barrier. Filled circles in figure 2 show the size dependence of the fission barriers calculated for the process $Sr_N^{2+} \rightarrow Sr^++Sr^+_{N-1}$. To calculate the fission barriers we use the procedure described in detail in our recent works [27, 28, 29]. The doubly charged strontium clusters with the number of atoms $N = 5$ and $8$ possess enhanced stability towards the neutral monomer evaporation as well as towards the Coulombic fission with ejection of a singly charged monomer.

For small doubly charged strontium clusters with the number of atoms $N \leq 7$ the neutral monomer dissociation energy, $D^{2+,0}_{N,1}$, exceeds significantly the fission barrier. Therefore, in this cluster size region fission prevails over neutral monomer evaporation. As the cluster size increases the fission barrier becomes comparable and exceeds the dissociation energy. In the size region $8 \leq N \leq 10$ the height of the fission barrier and $D^{2+,0}_{N,1}$ become almost equal resulting in the competition of the fission and the evaporation processes. For larger cluster sizes neutral monomer evaporation dominates over fission.

To find the critical size of stability at which clusters undergo Coulombic fission it is necessary to analyze the energy balance for all possible fission channels as a function of cluster size. Figure 2 shows the energy release, $D^{2+,+}_{N,P}$, as a function of different fission channels $P$ in the process $Sr_N^{2+} \rightarrow Sr^+_P+Sr^+_{N-P}$ for the doubly charged strontium clusters with the number of atoms up to $N = 11$. Coulombic fission takes place when the energy release is negative, which means that the final state of the system is energetically more favorable in comparison with the initial state of the parent cluster. We found that the
critical appearance size for the doubly charged strontium clusters is equal to \( N_{\text{app}} = 8 \). For the strontium clusters with \( N \geq 8 \) the energy release is positive for all fission channels. In this case cluster can decay via fission only if it possesses enough vibrational energy to promote the Coulombic fission.

The results of our ab initio calculations of the critical appearance size for doubly charged strontium clusters are in a good agreement with those derived from experiment \[4, 11\]. Doubly charged strontium clusters with number of atoms \( N \geq N_{\text{app}} \) are directly observed in the mass spectrum.

Figure 3 demonstrates strong influence of the shell effects on the fragmentation process \( \text{Sr}^{2+}_{N} \rightarrow \text{Sr}^{+}_{P} + \text{Sr}^{+}_{N-P} \). Thus, ejection of the singly charged dimer \( \text{Sr}^{+}_{2} \) is the energetically favorable channel of decay for the \( \text{Sr}^{2+}_{4}, \text{Sr}^{2+}_{7}, \text{Sr}^{2+}_{9} \) and \( \text{Sr}^{2+}_{11} \) clusters. For the \( \text{Sr}^{2+}_{10} \) cluster, the symmetric fission channel \( \text{Sr}^{2+}_{10} \rightarrow 2\text{Sr}^{+}_{5} \) is more favorable energetically. Singly charged strontium clusters always possess odd number of valence electrons and, thus, the interpretation of shell effects in terms of electronic shell closings is not straightforward. In this case, the enhanced stability of singly charged strontium clusters arises, when the electronic configuration of the cluster has one hole in or an extra electron above the filled shells \[18\]. This rule explains the manifestation of shell effects in fission of doubly charged strontium clusters.

The most complex situation with fission occurs when the cluster size lays in the “critical size” region. Thus, the \( \text{Sr}^{2+}_{7} \) cluster is the largest doubly charged strontium cluster which can spontaneously decay via the Coulombic fission. The following two channels \( \text{Sr}^{2+}_{7} \rightarrow \text{Sr}^{+}_{6} + \text{Sr}^{+} \) and \( \text{Sr}^{2+}_{7} \rightarrow \text{Sr}^{+}_{5} + \text{Sr}^{+}_{2} \) are allowed energetically. Fission via the ejection of the dimer \( \text{Sr}^{+}_{2} \) is much more favorable from the energetic viewpoint, however, in this case the system must overcome the higher fission barrier, as
it is seen from figure 4. Therefore the ejection of the singly charged monomer $Sr^+$ is the dominant fission channel for low cluster temperatures. As the temperature increases, the probability of ejection of the dimer $Sr_2^+$ grows. The similar effect was observed for the triply-charged strontium cluster $Sr_3^{3+}$ in [11].

The fission barrier maxima are located at small separation distances ($d_{\text{max}} \approx 9.5 \ \text{Å}$) just before the scission point. At such distances the parent cluster is strongly deformed. This shape deformation influences the dynamics of the fission and can induce, by dissipative effects, the ejection of a fast neutral atom [12].

In conclusion, experimentally measured dissociation energies are in agreement with those derived from our \textit{ab initio} calculations. We determine the cluster magic numbers possessing the enhanced stability towards monomer evaporation and fission. We demonstrate that the ionization of small strontium clusters results in the alteration of the magic numbers. The critical appearance size for the doubly charged strontium clusters determined theoretically is in a good agreement with experimental observations. Thermal promotion of the Coulombic fission for the $Sr_7^{2+}$ cluster is predicted.

**Acknowledgments**

The authors acknowledge support of this work by INTAS (grant No 03-51-6170) and the Russian Foundation for Basic Research (grant No 03-02-16415). We gratefully acknowledge support by the Frankfurt Center for Scientific Computing. A.L. expresses his gratitude to the Alexander von Humboldt Foundation for financial support.
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