LETTER TO THE EDITOR

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 \textit{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 Coulombic fission for the Sr\textsuperscript{2+}\textsubscript{7} cluster is predicted.

(Some figures in this article are in colour only in the electronic version)

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. Also, such investigations attract increased interest, because the general features of metal clusters decay and nuclear fission are quite similar.

In most cases neutral and singly charged clusters are intrinsically stable and their dissociation is endothermic. In this case an excess of energy is necessary to promote dissociation. This can be achieved by heating the cluster and making it thermally metastable. For neutral and singly charged clusters, decay into two fragments is a barrierless process, and its rate is defined by the corresponding dissociation energy. For multiply charged clusters, however, the decay into two charged daughter fragments usually involves overcoming a fission barrier which is a result of the interplay between Coulombic repulsion and cohesive forces.

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In this case, the fragmentation rate depends on the height of the fission barrier rather than on the dissociation energy. 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 on the cluster charge [7, 10, 11]. In this case evaporation is the dominant channel of cluster decay. For cluster sizes smaller than the critical size fission usually dominates over evaporation [3].

The most sophisticated situation arises when the cluster size approaches the ‘critical size’ region (see, e.g., [12] and references therein). It has been found experimentally that in this case the internal thermal excitation can influence fission channels and promote Coulombic fission [13]. On the other hand, fission into two charged fragments can stimulate an additional ejection of a neutral atom during or immediately after the system overcomes the fission barrier. Such an interplay between Coulombic fission and the evaporation processes has recently been observed [14].

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 Coulombic fission for the Sr$_2^{+}$ cluster and confirm the assumption made in [14] about the strong shape deformation of the fissioning Sr$_2^{+}$ cluster.

The experimental setup is similar to that used in previous works [14, 15]. 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., [16, 17] 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 [18]. To find the optimized geometry of a cluster we have used the procedure described in [19, 20]. 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 [21]. Calculations have been carried out with the use of the GAUSSIAN 03 software package [22]. The SDD basis set of primitive Gaussians has been used to expand the cluster orbitals (see, e.g., [16] and references therein).

The energetically preferred decay channel can be determined by the dissociation energy which is defined as

$$D_{N,P}^{Z,Q} = E_{tot}(M_{P}^{Q}) + E_{tot}(M_{N-P}^{Z-Q}) - E_{tot}(M_{Z}^{N}),$$

where $E_{tot}$ is the total energy of the metal cluster with the optimized geometry, Z and N are the charge and the size of the parent cluster, Q is the charge of the daughter fragment of size P. Figure 1 shows the monomer dissociation energies, for neutral and singly charged parent strontium clusters as a function of the cluster size. Filled squares and circles represent neutral monomer dissociation energies, $D_{N,1}^{0,0}$ and $D_{N,1}^{+0}$, calculated for neutral and singly charged parent strontium clusters, respectively. Crosses in figure 1 show the experimental results for neutral monomer dissociation energies $D_{N,1}^{0,0}$ of singly charged parent strontium clusters obtained in this work. The star presents the experimental value of $D_{2,1}^{+0}$ for the ionized strontium dimer from [23].
Figure 1. Monomer dissociation energies for neutral and singly charged Sr-clusters. Filled squares and circles: neutral monomer dissociation energies, $D_{0N}^0$ and $D_{0N}^1$, for the processes $\text{Sr}_N \rightarrow \text{Sr} + \text{Sr}_{N-1}$ and $\text{Sr}^+_N \rightarrow \text{Sr} + \text{Sr}^+_{N-1}$, respectively. Open circles: singly charged monomer dissociation energies, $D_{+N}^0$, for the process $\text{Sr}^+_N \rightarrow \text{Sr}^+ + \text{Sr}^+_{N-1}$. Crosses and star: experimental data.

The local maxima in the size dependence of the monomer dissociation energy, $D_{0N}^0$, at $N = 4, 7$ and 10 correspond to the most stable configurations of neutral Sr-clusters towards monomer evaporation $\text{Sr}_N \rightarrow \text{Sr} + \text{Sr}_{N-1}$. The same magic numbers have also been obtained from the analysis of binding energies of small neutral strontium [21] and magnesium [20] 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 trend in the property evolution of small strontium clusters [24]. Therefore, one can state that the most stable magic clusters $\text{Sr}_4$, $\text{Sr}_7$ and $\text{Sr}_{10}$ possess $N_{el} = 8, 14$ and 20 valence electrons respectively, which is in agreement with the deformed jellium model (see, e.g., [25–28] and references therein as well as discussion in [20]).

Open circles in figure 1 show the singly charged monomer dissociation energies, $D_{+N}^0$, calculated for singly charged parent strontium clusters. Figure 1 demonstrates that the evaporation of a charged monomer for singly charged strontium clusters, $\text{Sr}_N^+ \rightarrow \text{Sr}^+ + \text{Sr}_{N-1}$, is strongly suppressed in comparison with the evaporation of a neutral strontium atom, $\text{Sr}_N^0 \rightarrow \text{Sr} + \text{Sr}_{N-1}$. The singly charged strontium dimer $\text{Sr}_2^+$ 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 the cationic strontium dimer is more strongly bound. A similar effect has been discussed for cationic magnesium clusters in [20].

The local maxima in the size dependence of the neutral monomer dissociation energy, $D_{0N}^0$, for the $\text{Sr}_2^+$ and $\text{Sr}_7^+$ clusters indicate their enhanced stability towards monomer evaporation. Figure 1 clearly demonstrates that the single ionization of small strontium clusters results in alteration of the magic numbers. A similar change of the magic number from $N = 4$ for neutral to $N = 5$ for cationic magnesium clusters has been noted in our recent
work [20]. This fact can be explained by the manifestation of shell effects. The singly charged alkaline earth metal clusters always possess an 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 [20]. Thus the electronic configuration containing an extra electron becomes more favourable for Sr+.

The calculated values of $D_{2+0N,1}^1$ are in a good qualitative agreement with the experimental results. The 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 lie lower than those measured in the experiment. The results of geometry optimization of different isomer states of small strontium clusters will be discussed elsewhere [21].

Figure 2 shows the monomer dissociation energies for doubly charged parent strontium clusters as a function of cluster size. Filled and open triangles represent the neutral and singly charged monomer dissociation energies, $D_{2+0N,1}^1$ and $D_{2+0N,1}^1$, respectively. It is important to note that the decay of a doubly charged parent cluster into two singly charged daughter fragments usually involves overcoming a fission barrier caused by Coulombic repulsion, while evaporation is a barrierless process [3, 6]. Therefore, the values $D_{2+0N,1}^1$ 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 [29–31]. The doubly charged strontium clusters with
the number of atoms \( N = 5 \) and \( 8 \) possess enhanced stability towards neutral monomer
evaporation as well as towards 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, \( D_{2+}^{0} \), 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 \( D_{2+}^{0} \) 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 analyse the energy balance for all possible fission channels as a function of
cluster size. Figure 3 shows the energy release, \( D_{2+}^{P} \), as a function of different fission
channels \( P \) in the process \( \text{Sr}^{2+} \rightarrow \text{Sr}^{2+} + \text{Sr}_{N-P}^{+} \) for the doubly charged strontium clusters with
the number of atoms up to \( N = 11 \). The multiply charged clusters are intrinsically unstable
towards Coulombic fission when the energy release is negative, which means that the final
state of the system is energetically more favourable 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 clusters are intrinsically stable towards Coulombic
fission.

The results of our \textit{ab initio} calculations of the critical appearance size for doubly charged
strontium clusters are in good agreement with those derived from experiment [5, 13]. Doubly
charged strontium clusters with number of atoms \( N \geq N_{\text{app}} \) are directly observed in the mass
spectrum.

Figure 3 demonstrates the strong influence of the shell effects on the fragmentation
process \( \text{Sr}_{N}^{2+} \rightarrow \text{Sr}_{P}^{2+} + \text{Sr}_{N-P}^{+} \). Thus, the ejection of the singly charged dimer \( \text{Sr}_{2}^{+} \) is the
energetically favourable channel of decay for the \( \text{Sr}_{4}^{2+}, \text{Sr}_{7}^{2+}, \text{Sr}_{9}^{2+} \) and \( \text{Sr}_{11}^{2+} \) clusters. For
the \( \text{Sr}_{10}^{2+} \) cluster, the symmetric fission channel \( \text{Sr}_{10}^{2+} \rightarrow 2\text{Sr}_{5}^{+} \) is more favourable energetically.
Singly charged strontium clusters always possess an 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 [20]. 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 lies in the ‘critical size’ region. Thus, the Sr$_{2+}^7$ cluster is the largest doubly charged strontium cluster which can decay via Coulombic fission. The following two channels Sr$_{2+}^7 \rightarrow$ Sr$_{6}^+$ + Sr$^+$ and Sr$_{2+}^7 \rightarrow$ Sr$_{5}^+$ + Sr$_{2}^+$ are allowed energetically. Fission via the ejection of the dimer Sr$_{2}^+$ is much more favourable from the energetic view point; however, in this case the system must overcome the higher fission barrier, as 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. A similar effect was observed for the triply-charged strontium cluster Sr$_{3}^+$ in [13].

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 [14].

In conclusion, experimentally measured dissociation energies are in a good qualitative agreement with those derived from our 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 Coulombic fission for the Sr$_{2+}^7$ cluster is predicted.

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