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Dissociation and fission of small sodium and strontium clusters

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Abstract. Fission of charged small sodium and strontium clusters has been studied by the ab initio density functional theory methods. Dissociation energies and fission barriers have been calculated for all possible fission channels for the Na_{10}^{2+} and Sr_7^{2+} clusters. The dissociation energies and fission barriers have been analyzed as functions of the daughter fragment size.

PACS. 36.40.Qv Stability and fragmentation of clusters – 36.40.Wa Charged clusters – 31.15.Qg Molecular dynamics and other numerical methods

1 Introduction

The processes leading to instability and fission of metal clusters are of a fundamental importance in atomic cluster science, see, e.g., [1–8]. Investigation of fission of metal clusters provides a direct tool for studying intrinsic stability and binding forces of these objects. Such investigations attract increased interest, because of the fact that some of the general features in the decay of metal clusters and nuclei are quite similar being independent of the actual system studied, see, e.g., [9] and references therein.

We report the results of the ab initio molecular dynamics (MD) study of stability of doubly charged sodium, Na_{10}^{2+}, and strontium, Sr_N^{2+} ($N = 1...11$), clusters. Usually, stability of clusters is characterized by their dissociation energies. Indeed, for neutral and singly charged sodium and strontium clusters, decay into two fragments is a barrierless process, its rate defined by the corresponding dissociation energy. For doubly 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 [7, 10, 11]. In this case the fragmentation rate depends on the height of the fission barrier rather than on the dissociation energy.

We demonstrate that doubly charged strontium clusters are stable with respect to spontaneous fission for sizes $N \geq 8$. For the Sr_7^{2+} cluster there are only two fission channels for which the dissociation energies are negative, i.e. for which the decayed states are energetically favourable, $\mathrm{Sr}_7^{2+} \to \mathrm{Sr}_5^+ + \mathrm{Sr}_2^+$ and $\mathrm{Sr}_7^{2+} \to \mathrm{Sr}_6^+ + \mathrm{Sr}^+$. The fission barrier is lower for the unimolecular evaporation while the dissociation energy is more negative for dimer evaporation.

For the Na_{10}^{2+} cluster the dependences of the dissociation energy and fission barrier on the daughter fragment size have qualitatively similar behaviour. This similarity can be explained by electronic shell effects which favour forming fragments with filled and half-filled shells. However, as one may expect, the similarity is only qualitative, but not quantitative.

2 Calculations details

The optimized geometries of the clusters were determined with the use of the procedure described in [12–15]. To find the fission pathways we explore the multi-dimensional potential energy surface of the cluster. The global energy minimum on this surface characterizes the energetically preferred state of the system. In the case of metastable doubly charged clusters the global energy minimum corresponds to the system fragmented into two charged parts. The energetically preferred decay channel is determined by the dissociation energy which is generally defined as

$$D_{N,P}^{Z,Q} = E_{\mathrm{tot}}\left(M_P^{Q+}\right) + E_{\mathrm{tot}}\left(M_{N-P}^{(Z-Q)+}\right) - E_{\mathrm{tot}}\left(M_N^{Z+}\right), \tag{1}$$

where E_{tot} is the cluster total energy, Z and N are the charge and the size of the parent cluster while Q is the charge of the daughter fragment of size P.

The global energy minimum is located in the domain of the potential energy surface where the distance between the two fragments is infinitely large. There are other local minima at infinitely large distances between the

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fragments (at the "edges" of the potential energy surface) corresponding to other possible fission channels. The deepest local minimum on the potential energy surface located in its "center" part, where the two fragments are close, corresponds to the ground state of the cluster, while other local minima in the central part of the surface represent other (meta)stable isomer states.

In the potential energy surface approach the simulation of the fission process is reduced to finding a pathway on surface from a minimum in its central part to a minimum at the edge. The found pathway should minimize the energy barrier of the transition [16–18].

Calculation of the entire multi-dimensional potential energy surface is a formidable and, in fact, unnecessary task. Therefore, we start from the local minima in the "center part" of the potential energy surface, i.e. from the optimized geometries of a cluster [12,14]. We then choose the atoms the resulting fragments would consist of. The atoms chosen for a smaller fragment are shifted from their optimized locations in the parent cluster to a certain distance. Then, the multi-dimensional potential energy surface, its gradient and, consequently, forces with respect to the molecular coordinates are calculated. These quantities specify the direction along the surface in which the energy decreases the most rapidly and provide information for the determination of the next position of the atoms. If the fragments are removed not far enough from each other then the cohesive forces prevail over the repulsive ones and the fragments stick together forming the unified cluster again. Forming the unified cluster does not necessarily mean returning to the same point on the potential energy surface; it may happen that the system moves into another local minimum. This would correspond to changing the isomer state of the cluster. One can also find a potential barrier for such a transition. In the opposite situation the repulsive forces dominate and the fragments drift away from each other. The dependence of the total energy of the system on the fragments separation distance forms the fission barrier.

The calculations have been carried out with the use of the GAUSSIAN 98 software package [19]. The standard 6-31G(d) and 6-311G(d) basis sets of primitive Gaussian functions has been used to expand the orbitals of the sodium clusters (see [20] and references therein). This basis set takes into account electrons from all atomic orbitals, so that the dynamics of all particles in the system is taken into account. For strontium clusters we have used 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, and the SDD basis set of primitive Gaussians to expand the cluster orbitals. The hybrid Becke-type three-parameter exchange functional [21] paired with the gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP) [21–24] and the correlation functional of Perdew and Wang (B3PW91) [25, 26] have been used throughout this work, for sodium and strontium clusters, respectively. Such an approach has proved to be a reliable tool for the ab initio level studying the structure and properties of small sodium and strontium clusters [12,14,27].

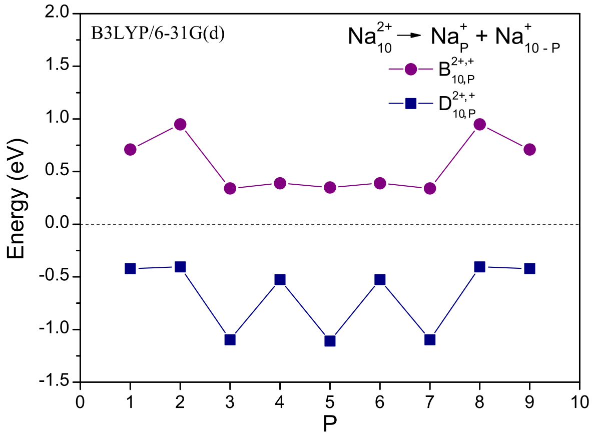

Fig. 1. Dissociation energy and fission barrier for the doubly charged Na_{10}^{2+} cluster as a function of the fission channel P.

3 Results of calculations

Figure 1 shows the dissociation energies, $D_{N,P}^{2+,+}$, and the fission barriers, $B_{N,P}^{2+,+}$, calculated for the reactions $Na_{10}^{2+} \rightarrow Na_P^+ + Na_{10-P}^+$, $P = 1...5$. These data provide essential information on the predominant fission channels in the system.

Dependence of the dissociation energy on daughter fragment size exhibits prominent odd-even oscillations. These features have a quantum origin appearing due to the spin pairing of the delocalized electrons. Therefore, clusters with even number of valence electrons are more energetically favourable. Closing of electron shells (which occurs when there are two, four or eight valence electrons) provides further stability to the system. Electronic configuration of a sodium atom is $1s^2 2s^2 2p^6 3s^1$, i.e. there is one valence electron per atom. Hence, the electronic shell effects suggest that the following pairs of the daughter fragments of the Na_{10}^{++} cluster are energetically preferred: (Na^+, Na_9^+), (Na_3^+, Na_7^+) and (Na_5^+, Na_5^+). For the last two pairs the dissociation energy is also minimal, in agreement with the results of the deformed jellium model, see, e.g., [28–33] and references therein.

However, the fission rate depends on the height of the fission barrier rather than on dissociation energy. The fission barriers $B_{10,P}^{2+,+}$, calculated by the method described in Section 2, are shown in Figure 1 with filled circles. The dissociation energy $D_{10,P}^{2+,+}$ and fission barrier $B_{10,P}^{2+,+}$ as functions of the fragments size do have some correlation in their behaviours, even though there is no direct correspondence between the two. Similarly to the prediction based on the dissociation energies, the calculated heights of the fission barriers suggest that the preferred fission channels are $Na_{10}^{2+} \rightarrow Na_3^+ + Na_7^+$ and $Na_{10}^{2+} \rightarrow 2Na_5^+$. In fact, the barrier heights for these channels are so close that the geometrical and statistical factors become of primary importance [34]. A complete analysis gives at high temperatures a small advantage to the asymmetric channel, $Na_{10}^{2+} \rightarrow Na_3^+ + Na_7^+$, in agreement with the other calculations [35,36] and experimental results [10].

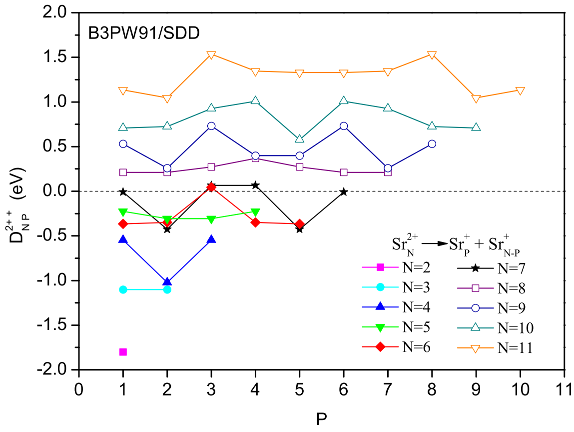

Fig. 2. Dissociation energy for different fission channels $\mathrm{Sr}_N^{2+} \to \mathrm{Sr}_P^+ + \mathrm{Sr}_{N-P}^+$ for the doubly charged Sr-clusters.

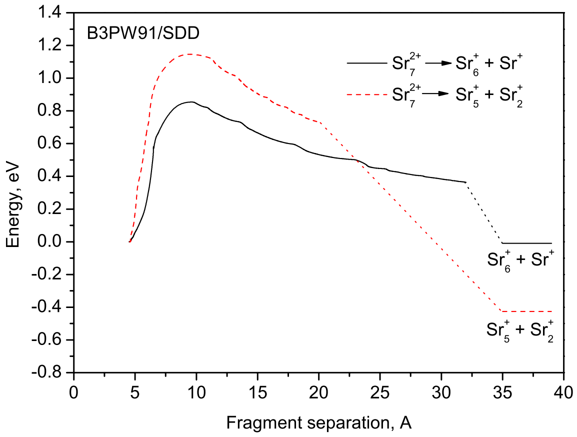

Fig. 3. Fission barriers for the Sr_7^{2+} cluster as a function of distance between the centers of mass of the fragments.

Figure 2 shows the dissociation energy, $D^{2+,+}_{N,P}$, as a function of different fission channels P in the process $\mathrm{Sr}_N^{2+} \to \mathrm{Sr}_P^+ + \mathrm{Sr}_{N-P}^+$ for the doubly charged strontium clusters with 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 $N_{app} = 8$. For the strontium clusters with $N \geq 8$ the energy release is positive for all possible fission channels. In this case cluster can decay via fission only if it possesses enough vibrational energy to promote 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 [37,38]. The doubly charged strontium clusters with number of atoms $N \geq N_{app}$ are directly observed in the mass spectra.

Figure 2 demonstrates a strong influence of the electronic shell effects on the fragmentation process $\mathrm{Sr}_N^{2+} \to \mathrm{Sr}_P^+ + \mathrm{Sr}_{N-P}^+$. Thus for the Sr_4^{2+}, Sr_7^{2+}, Sr_9^{2+} and Sr_{11}^{2+} clusters the ejection of the singly charged dimer Sr_2^+ is the energetically favorable channel of the decay. For the Sr_{10}^{2+} cluster the symmetric fission channel $\mathrm{Sr}_{10}^{2+} \to 2\mathrm{Sr}_5^+$ is more favorable energetically. The singly charged strontium clusters always possess odd number of valence electrons and, thus, the interpretation of the shell effects it terms of the electronic shell closure is rather questionable. However, in that case the enhanced stability of the singly charged strontium clusters can arise, when its electronic configuration has one hole in or an extra electron above the filled shells [13]. This assumption can explain the shell effects behavior in the fission of the doubly charged strontium clusters.

The most complex situation with fission occurs when the cluster size lays in the "critical size" region. Thus, the Sr_7^{2+} cluster is the largest doubly charged strontium cluster which can spontaneously decay via the Coulombic fission. The following two channels $\mathrm{Sr}_7^{2+} \to \mathrm{Sr}_6^+ + \mathrm{Sr}^+$ and $\mathrm{Sr}_7^{2+} \to \mathrm{Sr}_5^+ + \mathrm{Sr}_2^+$ are allowed energetically. Fission via the ejection of the dimer Sr_2^+ is much more favorable from the energetic view point, however, in this case the system must overcome the higher fission barrier, as it is seen from Figure 3. 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^+ rises. The similar effect was observed for the triply-charged strontium cluster Sr_{19}^{3+} in reference [38].

The fission barrier maxima are located at small separation distances ($d_{max} \approx 9.5$ 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 [39].

4 Conclusions

We have applied methods of density functional theory to studying fission of charged small sodium and strontium clusters. We calculated the dissociation energies and fission barriers for each decay channel. We have found that predictions of preferred fission channel based on analysis of the dissociation energies and fission barriers do not fully coincide. The theoretically determined critical appearance size for the doubly-charged strontium clusters is in a good agreement with experimental data. The thermal promotion of the Coulombic fission for the Sr_7^{2+} cluster is predicted.

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References

1. K. Sattler, J. Mühlbach, O. Echt, P. Pfau, E. Recknagel, Phys. Rev. Lett. **47**, 160 (1981)
2. T.P. Martin, J. Chem. Phys. **81**, 4426 (1984)

3. C. Bréchignac, Ph. Cahuzac, F. Carlier, J. Leygnier, Phys. Rev. Lett. **63**, 1368 (1989)
4. H. Haberland, *Clusters of Atoms and Molecules I and II* (Springer-Verlag, Berlin, 1994)
5. C. Bréchignac, Ph. Cahuzac, F. Carlier, M. de Frutos, Phys. Rev. B **49**, 2825 (1994)
6. U. Näher, S. Bjornholm, F. Frauendorf, C. Guet, Phys. Rep. **285**, 245 (1997)
7. C. Yannouleas, U. Landman, R.N. Barnett, in *Metal Clusters*, edited by W. Ekardt (Wiley, New York, 1999), p. 145
8. *Latest Advances in Atomic Cluster Collisions: Fission, Fusion, Electron, Ion and Photon Impact*, edited by J.-P. Connerade, A.V. Solov'yov (Imperial College Press, London, 2004)
9. *Metal Clusters*, edited by W. Ekardt (Wiley, New York, 1999)
10. C. Bréchignac, Ph. Cahuzac, F. Carlier, M. de Frutos, Phys. Rev. Lett. **64**, 2893 (1990)
11. C. Bréchignac, Ph. Cahuzac, F. Carlier, M. de Frutos, J. Leygnier, J.Ph. Roux, A. Sarfati, Comm. At. Mol. Phys. **31**, 361 (1995)
12. Il.A. Solov'yov, A.V. Solov'yov, W. Greiner, Phys. Rev. A **65**, 053203 (2002)
13. A. Lyalin, Il.A. Solov'yov, A.V. Solov'yov, W. Greiner, Phys. Rev. A **67**, 063203 (2003)
14. A. Lyalin, A.V. Solov'yov, W. Greiner, Phys. Rev. A (to be published)
15. I.A. Solov'yov, A. Lyalin, A.V. Solov'yov, W. Greiner, in reference [8], pp. 51–65
16. A.G. Lyalin, O.I. Obolensky, A.V. Solov'yov, Il.A. Solov'yov, W. Greiner J. Phys. B: At. Mol. Opt. Phys. **37**, L7 (2004)
17. A. Lyalin, O. Obolensky, Il. Solov'yov, A. Solov'yov, W. Greiner, Phys. Scripta T **110**, 319 (2004)
18. A. Lyalin, O. Obolensky, I.A. Solov'yov, A.V. Solov'yov, W. Greiner, in reference [8], pp. 157–168
19. M.J. Frisch et al., computer code GAUSSIAN 98, Rev. A. 11, Gaussian Inc., Pittsburgh, PA (1998)
20. J.B. Foresman, Æ. Frisch, *Exploring Chemistry with Electronic Structure Methods* (Pittsburgh, PA: Gaussian Inc, 1996)
21. A.D. Becke, Phys. Rev. A **38**, 3098 (1988)
22. A.D. Becke, J. Chem. Phys. **98**, 5648 (1993)
23. S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. **58**, 1200 (1980)
24. C. Lee, W. Yang, R.G. Parr, Phys. Rev. B **37**, 785 (1988)
25. J.P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche, H. Eschrig (Akademie Verlag, Berlin, 1991), p. 11
26. K. Burke, J.P. Perdew, Y. Wang, in *Electronic Density Functional Theory: Recent Progress and New Directions*, edited by J.F. Dobson, G. Vignale, M.P. Das (Plenum, 1998)
27. G.M. Wang, E. Blaisten-Barojas, A.E. Roitberg, T.P. Martin, J. Chem. Phys. **115**, 3640 (2001)
28. A. Matveentzev, A. Lyalin, I.A. Solov'yov, A.V. Solov'yov, W. Greiner, Int. J. Mod. Phys. E **12**, 81 (2003)
29. A.G. Lyalin, A. Matveentzev, Il.A. Solov'yov, A.V. Solov'yov, W. Greiner, Eur. Phys. J. D **24**, 15 (2003)
30. A.G. Lyalin, S.K. Semenov, A.V. Solov'yov, W. Greiner, Phys. Rev. A **65**, 023201 (2002)
31. A.G. Lyalin, A.V. Solov'yov, W. Greiner, Phys. Rev. A **65**, 043202 (2002)
32. A.G. Lyalin, S.K. Semenov, A.V. Solov'yov, N.A. Cherepkov, J.-P. Connerade, W. Greiner, J. Chin. Chem. Soc. **48**, 419 (2001)
33. A.G. Lyalin, S.K. Semenov, A.V. Solov'yov, N.A. Cherepkov, W. Greiner, J. Phys. B: At. Mol. Opt. Phys. **33**, 3653 (2000)
34. O.I. Obolensky, A. Lyalin, A.V. Solov'yov, W. Greiner, Phys. Rev. B (to be published)
35. B. Blaise, S.A. Blundell, C. Guet, R.R. Zope, Phys. Rev. Lett. **87**, 063401 (2001)
36. R.N. Barnett, U. Landman, G. Rajagopal, Phys. Rev. Lett. **67**, 3058 (1991)
37. M. Heinebrodt, S. Frank, N. Malinowski, F. Tast, I.M.L. Billas, T.P. Martin, Z. Phys. D **40**, 334 (1997)
38. C. Bréchignac, Ph. Cahuzac, N. Kébaïli, J. Leygnier, Phys. Rev. Lett. **81**, 4612 (1998)
39. C. Bréchignac, Ph. Cahuzac, B. Concina, J. Leygnier, Phys. Rev. Lett. **92**, 083401 (2004)