Geometrical and statistical factors in fission of small metal clusters

O. I. Obolensky,\textsuperscript{1,2} A. G. Lyalin,\textsuperscript{3} A. V. Solov'yov,\textsuperscript{1} and W. Greiner\textsuperscript{1}

\textsuperscript{1}Frankfurt Institute for Advanced Studies, Johann Wolfgang Goethe-University, Robert-Mayer Strasse 10, D-60054 Frankfurt am Main, Germany
\textsuperscript{2}A.F. Ioffe Institute, Politechnicheskaja str. 26, St. Petersburg 194021, Russia
\textsuperscript{3}Institute of Physics, St. Petersburg State University, Ulianovskaja 1, Petrodvorez, St. Petersburg 198504, Russia

Fission of metastable charged univalent metal clusters has been studied on example of \( \text{Na}^{2+}_{10} \) and \( \text{Na}^{2+}_{28} \) clusters by means of density functional theory methods. Energetics of the process, i.e. dissociation energies and fission barriers, as well as its dynamics, i.e. fission pathways, have been analyzed. The dissociation energies and fission barriers have been calculated for the full range of fission channels for the \( \text{Na}^{2+}_{10} \) cluster. Our data confirms the viewpoint that there is some correlation between these two quantities, which can often be explained by electronic shell effects. However, there is no quantitative correspondence between the dissociation energies and heights of fission barriers and the former can not serve as a good estimate for the latter. The impact of cluster structure on the fission process has been elucidated. The calculations show that the geometry of the smaller fragment and geometry of its immediate neighborhood in the larger fragment play a leading role in defining the fission barrier height: energy barriers for removing different combinations of atoms from the same parent cluster can vary greatly, while energy barriers for removing similar groups of atoms from similar places in different isomers of the parent cluster are usually similar. The present study demonstrates importance of rearrangement of the cluster structure during fission. The rearrangement can lower the fission barriers significantly. It may include forming a neck between the two fragments or fissioning via another isomer state of the parent cluster; examples of such processes are given. For several low-lying isomers of \( \text{Na}^{2+}_{10} \) cluster the potential barriers for transitions between these isomer states are calculated and compared with the corresponding fission barriers. These data suggest that there is a competition between ”direct” fission and fission going via intermediate isomer states of the parent cluster. An impact of the cluster geometry on the change of the system’s entropy due to fission is also discussed.

PACS numbers: 36.40.Qv, 36.40.Wa, 36.40.Mr, 61.46.+w

I. INTRODUCTION

Studying properties of charged clusters is of great interest both from theoretical and experimental viewpoints.\textsuperscript{2} In experiments, widely used clusters detection techniques proceed via ionization and subsequent mass spectrometry of clusters (see Refs.\textsuperscript{2,3} for a review and references). On the other hand, charged clusters behaviour presents one of the instances of a long standing fundamental theoretical problem of stability of complex systems since charged clusters can be found in stable, metastable or unstable states, depending on cluster size and excessive charge. Metal clusters are especially attractive subject of study because fission of charged metal clusters provides close analogies to the corresponding processes in nuclear systems.

For semi-quantitative classification of stability of charged metal clusters it is convenient to use a fissility parameter introduced by Lord Rayleigh more than a century ago while he was investigating stability of small charged liquid droplets. The fissility parameter is defined as ratio of the Coulomb to surface energies of the drop, \( X = E_{\text{Coul}}/2E_{\text{Surf}} \). For spherical sodium clusters, \( X \approx 2.5Q^2/N \) (\( Q \) and \( N \) are the cluster charge and size, respectively). For \( X \ll 1 \) clusters are stable, for \( X \gg 1 \) clusters are unstable and fragment by the Coulomb explosion. For \( X \sim 1 \) clusters are found in metastable states and must overcome a potential barrier in order to fission. As in many other recent studies,\textsuperscript{4,5,6,7,8,9,10,11} we focus on the latter situation and present results of our all-electrons density functional calculations which help to achieve better understanding of various aspects of fission of metastable charged metal clusters. We use sodium clusters, well studied experimentally, as a sample revealing general properties of univalent metal clusters.

Within the Born-Oppenheimer approximation, we employ density functional theory methods for calculating the electronic structure for every given configuration of the nuclei. Our approach differs from the standard technique of molecular dynamics simulations. In our calculations we explore the multi-dimensional potential energy surface of a cluster system in order to find the local minima on this surface, corresponding to different cluster isomers. The potential energy surface also allows to determine the optimal fission pathways which minimize the fission barriers.

We begin with calculating the energetics of the fission process. We present the dissociation energies and fission barriers for all possible fission channels for the \( \text{Na}^{2+}_{10} \) cluster for which the excessive charge is distributed between the
daughter fragments, $Na_{10}^{2+} \rightarrow Na^{+}_{p} + Na_{N-p}^{+}$, $P = 1.5$. Such channels are energetically more favourable compared to the evaporation channels in which a neutral and double charged fragments appear in the final state.

The dissociation energies is an important characteristic of the fission process, useful in assessing stability/instability of a particular cluster. Comparison of the dissociation energies and fission barriers shows that there is some correlation between the two quantities. This correlation can often be explained by electronic shell effects which favour forming fragments with filled and half-filled shells. However, as one may expect, the correlation is only qualitative, and therefore dissociation energies cannot serve as an easy-to-calculate, convenient tool for making reliable predictions concerning the fission process (e.g. predictions of the preferred fission channel or branching ratios between different channels) and one needs to find fission barrier heights.

On the other hand, even knowledge of the fission barrier heights is sometimes not sufficient for predicting the preferred fission channel. This is the case for the dominant asymmetric, $Na_{10}^{2+} \rightarrow Na^{+}_{p} + Na_{N-p}^{+}$, and symmetric, $Na_{10}^{4+} \rightarrow 2Na^{2+}$, fission channels for the $Na_{10}^{4+}$ cluster. Considerations based on electronic shell effects suggest that these two channels ought to be the favoured ones. The accurate ab initio calculations confirm this conclusion, but it turns out that the barrier heights for these channels are so close that one needs to take into account geometrical and statistical factors, as discussed below (section III B).

Our approach permits also studying the dynamics of the fission process. Having calculated the multi-dimensional energy surface we were able to determine the optimal dynamic pathways of the fission for all the channels considered. Analysis of the data suggests that significant rearrangement of the cluster structure often accompanies fission.

One can distinguish between two main types of such rearrangement. The first one is a rearrangement of the cluster structure without significant change in distance between the centers of mass of the prospective fragments. This type of rearrangement takes place before the actual separation of the fragments begins and it is, in fact, a transition to another isomer state of the parent cluster. The second type of rearrangement is characterized by existence of a super-molecule-like intermediate state in which the fragments are sufficiently separated from each other, but connected by a "neck". A similar necking phenomenon is known for nuclear fission. Necking allows for great reduction in the overall height of the fission barrier and is responsible for a double humped form of the barrier. In dynamical simulations necking can be observed as an elongation of the cluster shape during fission.

The first type of rearrangement implies that there is a competition between one-step ("direct" fission) and two-step (fission via an intermediate isomer state) processes. Therefore, in order to make predictions concerning the fission activation energy and fission pathway for a given cluster isomer one has first to find the energy barrier for the direct fission of the given isomer and then to compare the height of this barrier with the heights of the fission barriers for other low lying isomers. The differences in the isomer energies and potential barriers between the isomers have also to be taken into account. We present such analysis for the $Na_{10}^{2+}$ cluster.

Accounting for geometry of a fissioning cluster necessitates an extra care in calculating the fission barriers, since removing different combinations of atoms requires overcoming different barriers. In other words, different combinations of atoms are not necessarily equivalent in respect to fission. Depending on the symmetry group of a cluster there may exist the groups of atoms with the same potential energy barriers. When searching for the fission barrier of a cluster one needs to identify all such groups of atoms and choose the group with the lowest barrier.

It is sometimes also possible to identify geometrically similar groups of atoms, belonging to different isomers, for which the energy barriers are very close, even though the overall geometries of the isomers can be quite unalike. This suggests that the geometry of the smaller fragment and geometry of its immediate neighborhood in the parent cluster play a leading role in defining the energy barrier height.

Accounting for cluster geometry, which leads to non-equivalence of different combinations of atoms may have a further important impact on the way how the change of the system entropy due to fission should be calculated. It has been argued that accounting for an entropy change contribution to the free energy of the system is necessary for correct description of the temperature and size dependences of the branching ratios between different fission channels, while purely energetic considerations based on fission barrier heights fail. The entropy change is, in fact, a change in the statistical weight of the initial and final states of the system. In order to calculate the change in the statistical weight one has to count the change in number of combinations out of which the initial and final states of the system are composed. The non-equivalence of different combinations of atoms leads to replacement of the binominal law, used when all the atoms in a cluster are equivalent, by a more accurate treatment, which has to take into account particular geometry of a given isomer. We base such a treatment on counting the number of equivalent combinations of atoms with the minimum potential energy barrier. The type of statistics to be used when calculating the change of the system’s entropy is determined by the cluster temperature. At high temperatures the cluster is melted and does

---

1 This is, of course, sensible for cluster temperatures below the melting point only. For temperatures above the melting point the atoms in clusters do not have stationary positions and one cannot speak of a certain geometry of a cluster.
not possess a certain structure. In this situation the purely combinatorial approach is fully justified. Conversely, at low temperatures a more detailed account of the cluster structure is needed.

We note, that the kinds of studies mentioned above are beyond the scope of simpler approaches which do not take into account ionic structure of clusters. In such approaches, e.g. in the jellium model, one may speak of, say, prolate and oblate jellium shapes as of different isomers, but this does not reflect all the variety of energies and geometries of stable cluster isomers.

II. SIMULATION DETAILS

A. General formalism

We utilize the methods of density functional theory (DFT) within the Born-Oppenheimer scheme. In accord with the DFT prescriptions we iteratively solve the Kohn-Sham equations\textsuperscript{19}

\[
\left( \frac{p^2}{2} + U_i + V_H + V_{xc} \right) \psi_i = \varepsilon_i \psi_i, \tag{1}
\]

where the first term corresponds to the kinetic energy of an electron, \(U_i\) describes the attraction of the \(i^{th}\) electron to the nuclei in the cluster, \(\psi_i\) is the electronic orbital, \(V_H\) is the Hartree part of the inter-electronic interaction,

\[
V_H(r) = \int \frac{\rho(r')}{|r-r'|} dr', \tag{2}
\]

\(\rho(r)\) is the electron density, \(V_{xc}\) is the local exchange-correlation potential defined as the functional derivative of the exchange-correlation energy functional

\[
V_{xc} = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}. \tag{3}
\]

where the exchange-correlation energy is partitioned into two parts, referred to as exchange and correlation parts:

\[
E_{xc}[\rho] = E_x(\rho) + E_c(\rho). \tag{4}
\]

There is a variety of exchange-correlation functionals in the literature. We have used the three-parameter Becke-type gradient-corrected exchange functional with the gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP). For the explicit form of this functional we refer to the original papers\textsuperscript{20,21,22}. The B3LYP functional has proved to be a reliable tool for studying the structure and properties of small sodium clusters. It provides high accuracy at comparatively low computational costs. For a discussion and a comparison with other approaches, see Refs.\textsuperscript{23,24}.

B. Simulation procedure

We employ a procedure somewhat different from the usual molecular dynamics simulations techniques. In our calculation we explore the multi-dimensional potential energy surface of the cluster. For each point on this surface we solve Eq. 1 for the corresponding geometry of the atomic nuclei by expanding the cluster orbitals into the basis sets of primitive Gaussian functions\textsuperscript{25} with the use of the GAUSSIAN 03 software package\textsuperscript{26}.

The 6-31G(d) and LANL2DZ basis sets of the Gaussian functions have been used. The 6-31G(d) basis set has been used for simulations involving the \(Na^{2+}\) cluster. This basis set expands all the atomic orbitals, so that the dynamics of all particles in the system is accounted for. For the \(Na_{18}^{2+}\) cluster we have used the more numerically efficient LANL2DZ basis, for which valent atomic electrons move in an effective core potential (see details in Ref.\textsuperscript{25}). The accuracy and consistency of the calculations is proved by the correct asymptotics of the total energy of the system at large separation distances, i.e. the total energy of the system at large separation distances equals to the sum of the total energies of the charged isolated fragments (calculated separately) and the Coulomb repulsion energy. For certain fission channels we have also compared the fission barriers obtained with the use of different basis sets (6-311G(d), 6-31G(d), LANL2DZ) and confirmed that our results do not depend on the choice of the basis set.

The global minimum on thus found multi-dimensional potential energy surface corresponds to the energetically preferred state of the system. In the case of metastable doubly charged clusters the global minimum corresponds
to the system, fragmented into two charged parts. The fission channel corresponding to the global minimum can be determined from the dissociation energies which can be generally defined as

\[
D_{N,P}^{Q,P'} = E_{P'}^Q + E_{N-P}^{Q'-Q} - E_N^Q, 
\]

where \(N\) and \(Q\) are the size and the charge of the parent cluster, \(P\) and \(Q'\) are the size and the charge of one of the daughter fragments, \(E_M^W\) is the total energy of a cluster of size \(M\) and charge \(W\). The global 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 fragments (at the “edges” of the potential energy surface) corresponding to other possible fission channels. The deepest local minimum on the potential energy surface which is located in the “center” part of the surface, where the two parts of the system are close, corresponds to the ground state of the cluster, while other local minima in the center part of the surface represent other (meta)stable isomers.

In this potential energy surface approach the simulation of the fission process comes to finding a pathway on the system’s multi-dimensional potential energy surface from a minimum in the center part of the surface to a minimum at its edge. The found pathway must minimize the energy barrier for the transition.

In simulation of the fission process we start from the optimized geometry of a cluster (for details of the geometry optimization procedure see Ref. 23) and 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 forces with respect to the molecular coordinates are calculated. These quantities specify the direction along the surface in which the energy decreases most rapidly and provide information for the determination of the next place for placing 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 gets into another local minimum. This would correspond to changing the isomer state of the cluster. Correspondingly, one can find a potential barrier for such transition. If the fragments are far enough from each other, 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 potential energy barrier for a given pathway. Hence, finding the fission barrier is equivalent to finding the pathway with the lowest potential energy barrier.

Determining fission barriers is a computationally demanding task which requires a lot of computer resources. Currently, it is not feasible to study the multi-dimensional potential energy surface in fine details even for relatively small clusters. Therefore, there is no guarantee that the found fission pathways provide the lowest fission barriers. Even small deviation from the found pathway may result in a slight decrease in the fission barrier height. We estimate accuracy of the fission barrier heights presented in this paper to be 0.02-0.04 eV. Further calculations could allow to obtain a more accurate profile of the fission barrier and to determine the fission barrier height more precisely. However, the accuracy of theoretical models used nowadays to describe the experimental results, as well as the accuracy of the experimental data itself, make such refinements unneeded.

There is also a possibility that we have overlooked a completely different fission pathway which would make the fission barrier even lower. In fact, this was the case with the fission barrier for the dominant asymmetric fission channel for the \(Na_{10}^{2+}\) cluster, \(Na_{10}^{2+} \rightarrow Na_3^{+} + Na_7^{2+}\). Our previous calculations\(^2\) had resulted in the fission barrier of about 0.5 eV for this channel. This was in a good agreement with the results of other molecular dynamics simulations\(^5,15\). However, a more detailed study of the multi-dimensional potential energy surface performed in this work which included a more complete analysis of various possible rearrangements of the cluster structure in the course of fission allowed us to find a lower fission barrier for this channel, equal to 0.34 eV.

### III. RESULTS AND DISCUSSION

#### A. Fission energetics: dissociation energies and fission barriers

The energetics of the fission process is characterized by the dissociation energies \(D_{N,P}^{Q,P'}\) and the fission barriers \(B_{N,P}^{Q,P'}\) (here \(N\) and \(Q\) are the size and the charge of the fissioning cluster and \(P\) and \(Q'\) denote the size and the

\(^2\) For example, a calculation of one point of the system’s potential energy surface for the \(Na_{10}^{2+}\) cluster takes about a minute on a Pentium Xeon processor if only valent electrons are considered and about twenty minutes if all 108 electrons are accounted for.
TABLE I: The dissociation energies $D^{2+,-}_P$ and fission barrier heights $B^{2+,-}_P$ (in eV) for various fragment sizes $P$ for the fission of the $Na^{2+}_{10}$ cluster, $Na^{2+}_{10} \rightarrow Na^+_P + Na^{+}_{10-P}$.

| $P$ | $D^{2+}_P$ (this work) | $D^{2+}_P$ (Ref. 12) | $D^{2+}_P$, (Ref. 13) | $D^{2+}_P$, (Jellium model) |
|-----|------------------------|----------------------|-----------------------|---------------------------|
| 1   | -0.38      | 0.49     | 0.69     | 0.16                        |
| 2   | -0.37      | 0.52     | 0.67     |                             |
| 3   | -1.07      | 0.34     | 1.03     |                             |
| 4   | -0.52      | 0.39     | 0.71     |                             |
| 5   | -1.11      | 0.35     | 0.35     |                             |

For metastable clusters, fission barrier is an important characteristic of the fission process, while dissociation energy plays a smaller role. The parameters of the fission barriers largely define many experimentally observable characteristics of the process, including branching ratios between different fission channels, fission time, etc. The dissociation energies are of limited use for metastable clusters. Their negative signs show that the clusters are unstable in respect to the corresponding fission channels. One could hope that easy-to-calculate dissociation energies could serve as quick qualitative estimates of fission barriers, since calculations of fission barriers are much more laborious and require more computer resources.

FIG. 1: (Color online) The fission barriers for the different channels of fission of the $Na^{2+}_{10}$ cluster, $Na^{2+}_{10} \rightarrow Na^+_P + Na^{+}_{10-P}$. The zero level of energy is chosen equal to the energy of the ground isomer state (with distorted $T_d$ symmetry, denoted in the paper $T_d^{(1)}$) of the cluster. The initial separation distances correspond to the distances between the centers of masses of the prospective fragments and, consequently, are finite, so that the barriers do not start at the origin.

To answer this question, we have determined the dissociation energies and fission barriers for the full range of fission channels for the $Na^{2+}_{10}$ cluster,

$$Na^{2+}_{10} \rightarrow Na^+_P + Na^{+}_{10-P}, \quad P = 1.5$$

The obtained fission barriers are plotted in Fig. 1. The fission barrier heights and the dissociation energies as functions of fission channel are presented in Fig. 2 and also summarized in Table I.

Unfortunately, although there is some correlation in behaviour of the two functions, there is no direct correspondence between them. Therefore, the dissociation energy can not serve as a quick estimate for the fission barrier height and
one needs to carry out the full calculation in order to find the fission barrier. Only after that one can make reliable predictions concerning the fission process.

The correlation in dependence of the dissociation energy and fission barrier height on the size of the daughter fragment can be explained by electronic shell effects which favour forming fragments with filled and half-filled shells. Indeed, the barrier maxima are located at distances comparable to or exceeding the sum of the resulting fragments radii, that is not far from the scission point. At such distances the interaction between the fragments, apart from Coulombic repulsion, is mainly determined by the electronic properties of the system (and also by the cluster geometry in the immediate vicinity of the scission point), rather than by the details of the ionic structure of the bulk of the fragments.

Indeed, the \textit{a priori} electronic shell considerations suggest that, for example, for the \( \text{Na}_{2+}^{10} \) cluster two fission channels, namely, \( \text{Na}_{2+}^{10} \rightarrow \text{Na}_{7}^{+} + \text{Na}_{3}^{+} \) and \( \text{Na}_{2+}^{10} \rightarrow 2\text{Na}_{5}^{+} \), dominate. Our calculations confirm this conclusion, but it turns out that the barrier heights for these channels are so close that the geometrical and statistical factors become of primary importance. We discuss the impact of geometry of the cluster on the fission process in the next subsection.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fission.png}
\caption{(Color online) The fission barrier heights \( B_{2+}^{10,P} \) (circles) and dissociation energies \( D_{2+}^{10,P} \) (squares) as functions of the fragment size \( P \) for the fission of the ground state of the \( \text{Na}_{2+}^{10} \) cluster, \( \text{Na}_{2+}^{10} \rightarrow \text{Na}_{7}^{+} + \text{Na}_{3}^{+} \).}
\end{figure}

\textbf{B. Impact of the cluster geometry on fission process}

Detailed analysis of cluster geometry in the course of fission allows for deeper understanding of the process. It, however, brings in two issues which must be properly accounted for. The first one is the fact that the different combinations of equal number of atoms are not necessarily equivalent for a given cluster geometry, and the potential barriers to be overcome in order to remove these combinations of atoms from the parent cluster are quite likely to differ. The second issue is that not always “direct” fission (i.e. straightforward removing some combination of atoms from the parent cluster) has lower potential barrier than fission going via an intermediate isomer state of the parent cluster or via formation of a super-molecule-like necked structure. This latter issue will be discussed in detail in the next subsection.

The problem of finding the lowest fission barrier is simplified in many cases by the presence of a symmetry in a cluster geometry which reduces the number of non-equivalent combinations of atoms participating in the fission process.

Let us consider fission of the \( \text{Na}_{2+}^{10} \) cluster. Its ground state isomer has a slightly distorted symmetry of the \( T_{d} \) point symmetry group\footnote{23} and can be described as a pyramid, see Figure 4. We will denote this isomer as \( T_{d}^{(1)} \). Four atoms in the isomer are located in the vertices of the pyramid and six are in the centers of the edges. All the edge and all the vertex atoms can be considered equivalent. Therefore, when considering the fission channel \( \text{Na}_{2+}^{10} \rightarrow \text{Na}_{5}^{+} + \text{Na}_{5}^{+} \) it
TABLE II: The potential energy barrier heights for removing various combinations of two atoms from the parent $Na_{10}^{2+}$ cluster, see the text for explanations.

|     | VV  | VE1 | VE2 | EE1 | EE2 |
|-----|-----|-----|-----|-----|-----|
| 1.63| 0.97| 1.11| 0.97| 1.18| eV  |

suffices to find two energy barriers only rather than calculating a barrier for each atom. The potential energy barrier height for removing an atom from an edge of the cluster is 0.85 eV, while it is 0.71 eV for removing an atom from a vertex. Hence, the fission barrier height for the fission channel is 0.71 eV.

![Diagram](Image)

FIG. 3: (Color online) The geometry of the ground state isomer of the $Na_{10}^{2+}$ cluster. It has no point symmetries, but its structure is, in fact, a pyramid ($T_d$ symmetry group), slightly distorted due to the Jahn-Teller effect.

There are more energy barriers which need to be calculated for the $Na_{10}^{2+} \rightarrow Na_8^{+} + Na_2^{+}$ channel. Totally, there are 45 combinations of two atoms out of ten. Fortunately, there are only five energy barriers which are to be calculated. Indeed, two atoms which are to be removed from the parent cluster can be taken either both from the vertices, or both from the edges, or one atom from a vertex and one from an edge. All combinations of two atoms taken from the vertices are equivalent. There are six such combinations which we will denote as VV. Twenty four combinations of two atoms in which one atom comes from a vertex and one from an edge can be further divided into two equal subgroups. In the first subgroup (VE1) atoms belong to the same edge while in the second subgroup (VE2) they do not. Fifteen combinations of atoms from the edges are also divided into two subgroups. The first one contains atoms belonging to the same face of the pyramid (twelve combinations, EE1) and the second group (EE2) contains the combinations of atoms from the different pyramid faces. The heights of the energy barriers for these five groups are summarized in Table II.

One can see from Table II that in the case of the $Na_{10}^{2+} \rightarrow Na_8^{+} + Na_2^{+}$ channel, the two atoms which are to be removed from the parent cluster in the fission process must be taken either from a vertex and the middle of an edge originating from this vertex or from the middles of two edges belonging to the the face of the pyramid. Other combinations of atoms have higher potential barriers and do not participate, as a good approximation, in the process. In other words, the daughter fragment should contain certain classes of combinations of atoms only, in order to obtain a lower potential energy barrier. Our analysis shows that this conclusion is also valid for other fission channels and parent cluster isomers. Typically, the combinations which provide the minimum energy barrier include neighbouring atoms located in a part of the parent cluster which can be the most easily removed.

On the other hand, it is sometimes possible to identify geometrically similar groups of atoms belonging to different isomers for which the energy barriers are very close, even though the overall geometries of the isomers are not similar and can even be quite unlike. This fact taken in conjunction with the non-equivalence of different combinations of atoms within one isomer state, suggests that the geometry of the smaller fragment and geometry of its immediate neighborhood in the larger fragment play a leading role in defining the energy barrier height. We can demonstrate this by comparing energy barriers for removing similar groups of atoms from similar places in the parent cluster for two different isomer states of the $Na_{10}^{2+}$ cluster. One of these isomers possesses the symmetry of $C_{4v}$ point symmetry group and another one is of $D_{4d}$ symmetry. The isomers geometries are depicted in Figure 4, the groups of atoms to be removed are shown in black color. The resulting barriers are presented in Figure 5. It is seen from the figure that the barriers are similar not only in height but also in shape. This can be explained by similarities of the geometries.
of the prospective smaller fragments, similarities in the immediate neighbourhoods of the smaller fragments, and also by similarities in the charge distribution in the isomers, and by absence of additional structure rearrangements in the course of fission.

FIG. 4: (Color online) Two isomers of the $Na_{10}^{2+}$ cluster. From left to right: an isomer of $C_{4v}$ point symmetry group (nicknamed iso1414); an isomer of $D_{4d}$ point symmetry group (nicknamed iso1441). The similar combinations of three atoms which provide very close fission barriers are marked with black color.

FIG. 5: (Color online) Energy barriers for removing similar combinations of three atoms (marked by black color in Figure 4) from the two different isomers of the $Na_{10}^{2+}$ cluster. The barriers plotted versus distance between the centers of mass of the fragments. The curve with the stars corresponds to the isomer with the symmetry of $C_{4v}$ point group (iso1414); the curve with the diamonds corresponds to the isomer possessing the symmetry of $D_{4d}$ point group (iso1441). Note, that energies are measured from the energy of the initial state of the corresponding isomer, i.e. we plot $E - E_{C_{4v}(D_{4d})}$, where $E$ is the total energy of the system and $E_{C_{4v}(D_{4d})}$ are the energies of the iso1414 and iso1441 isomers, respectively.

The fact of inequivalence of different combinations of atoms in a cluster isomer may have an important impact on various characteristics of the fission process such as branching ratios between different fission channels and their temperature dependence.
It has been argued theoretically and shown experimentally that dominant fission channels and the branching ratios between different channels are not governed by purely energetic considerations but also by the free energy change which takes into account the different combinations of atoms which constitute the fragments.\cite{17,18} Accounting for an entropy change contribution to the free energy of the system was necessary for correct description of the experimental results. The branching ratio $I_2/I_1$ between two channels is then defined by the difference in the fission barrier heights $\Delta B \equiv B_{Q,Q'}^{Q,Q'} - B_{Q,Q'}^{Q,Q'}$ and by the entropy change $\Delta S$ of the system:

$$\frac{I_2}{I_1} = f \exp\left(\frac{\Delta S}{k} - \frac{\Delta B}{kT}\right).$$

(7)

Here $k$ is the Boltzmann constant, $T$ is the cluster temperature, $f$ is a frequency factor. This factor arises due to different frequencies $\omega$ of oscillations in the modes leading to fragmentation of the cluster in different fission channels. Roughly speaking, the fragmentation occurs when due to a fluctuation energy concentrates in a single oscillation mode in the amount sufficient for overcoming the fission barrier. Fission would be more probable if the frequency of oscillations in this mode is higher, since then the system would "attempt to fragment" more frequently. Hence, in a crude approximation $f \sim \omega_2/\omega_1$. If one assumes that the potential surfaces for both modes can be approximated by parabolas with same curvatures, then the ratio of the frequencies of oscillations will depend only on the reduced masses $\mu$ of the pairs of the prospective fragments, $f \sim \mu_1/\mu_2$. For the dominant asymmetric and symmetric fission channels for the $Na^{2+}_{10}$ cluster the frequency factor $f$ is about 1.1, so we will neglect its influence and put $f = 1$. Of course, this factor can be estimated more accurately. In order to do that one has to determine all the normal modes of oscillations of the parent cluster, to represent the oscillations leading to the given fission channel via a combination of normal mode oscillations and calculate the probability that enough energy would fluctuate into these normal modes. Such an analysis would go beyond the aims of the current work and can be a subject of a separate study. We now focus on the influence of the cluster structure on the way how the system’s entropy should be calculated.

The entropy change entering the equation (7) is, in fact, a change in the statistical weight of the initial and final states of the system. In order to calculate the change in the statistical weight $\Gamma$ one has to count the change in number of combinations out of which the initial and final states of the system are composed,

$$\Delta S = k \ln \Gamma_2 - k \ln \Gamma_1 = k \ln \frac{\Gamma_2}{\Gamma_1}. \quad (8)$$

For high temperatures all atoms can be considered equivalent and the number of combinations of $P$ atoms out of $N$ is given by the binominal coefficient, $\Gamma = \binom{N}{P}$, so that

$$\Delta S = k \ln \frac{N!}{(N - P_2)!P_2!} - k \ln \frac{N!}{(N - P_1)!P_1!} = k \ln \frac{(N - P_1)!P_1!}{(N - P_2)!P_2!}. \quad (9)$$

The non-equivalence of different combinations of atoms requires replacement of the binomial law, used in Ref.\cite{18} for high temperature regime when all the atoms in cluster are equivalent, by a more detailed treatment, which has to take into account particular geometry of a given isomer. Such a treatment should be based on counting the number of equivalent combinations of atoms which provide the minimum potential energy barrier (for low temperatures it is justified to assume that fission proceeds only through the pathway with the minimum energy barrier). This change in the statistics may lead to significant change in the branching ratios between fission channels and to the alteration of the predominant channel.

For example, symmetric $Na_{10}^{2+} \rightarrow 2Na_{5}^{2+}$ and asymmetric $Na_{10}^{2+} \rightarrow Na_{7}^{+} + Na_{3}^{+}$ channels have very similar fission barriers, and one would expect that these two processes would occur with similar probabilities. The difference in the barriers heights of 0.01 eV (see Table 1) would lead to the branching ratio between the symmetric and asymmetric channels approximately equal to 2:3 at room temperature and 1:1 at higher temperatures. If one adopts the statistics based on the binomial law, the symmetric channel becomes the preferred fission channel, since there are 252 combinations of five atoms out of ten and only 120 combinations of three atoms out of ten. Therefore, using the binominal statistics leads one to conclude that the symmetric channel should prevail in experimental mass spectra.

If, however, different combinations of atoms in the parent cluster are considered non-equivalent, then one needs to identify carefully the combinations of atoms which provide the lowest separation barrier and to count the numbers of such combinations. In the asymmetric channel the lowest barrier is obtained when an atom from a vertex and two neighbouring atoms from the middles of the edges which cross at the vertex are removed. There are totally 12 such combinations of atoms. In the symmetric channel four atoms are removed from the top of the pyramid and one from the middle of the edge in the base of the pyramid. There are 12 such combinations, too. Hence, the statistics which accounts for the cluster geometry leads one to conclude that both channels statistically are equally probable, so the branching ratio is governed by the heights of the barriers only, i.e. the asymmetric channel prevails.
The statistics based on the binominal law is more adequate for high temperatures when a cluster is melted and does not possess a certain structure\(^3\). To the contrary, at low temperatures, when the cluster structure is important, the alternative statistics is more appropriate.

One can make an important conclusion based on these considerations regarding the particular case of fission of the Na\(^{2+}_{10}\) cluster. Namely, at high temperatures the symmetric channel is the preferred fission channel, while at low temperatures when the cluster structure comes into play the asymmetric channel slightly dominates.

C. Fission dynamics: fission pathways and rearrangement during fission

The potential energy surface approach allows one to study the dynamics of the fission process. Having calculated the multi-dimensional potential energy surface for Na\(^{2+}_{10}\) and Na\(^{2+}_{18}\) clusters we were able to determine the optimal pathways for all the considered fission channels, i.e. we have determined the coordinates of all atoms which minimize the total cluster energy on each step of the simulation for each fission channel.

We have observed that often fission barrier can be greatly lowered by drawing the fission pathway via a local minimum on the potential energy surface. In other words, fission can proceed via formation of intermediate isomers. This requires extra rearrangement of the cluster structure as compared to a more straightforward fission pathway.

One can distinguish between two main kinds of such rearrangement\(^{12}\) The first one is rearrangement of the cluster structure without significant change in distance between the centers of mass of the prospective fragments. This type of rearrangement takes place before actual separation of the fragments begins and it is, in fact, a transition to another isomer state of the parent cluster. The second type of rearrangement is characterized by existence of a super-molecule-like intermediate state in which the fragments are sufficiently separated from each other, but connected by a "neck"\(^{2,13,14,15}\). A similar necking phenomenon is known for nuclear fission\(^{16}\). Necking is responsible for a double humped form of the fission barrier. In dynamical simulations necking can be observed as an elongation of the cluster shape during fission\(^{5,9}\).

For the Na\(^{2+}_{10}\) cluster, the rearrangement of the second type takes place in the three out of five fission channels which can be easily recognized by the double humped form of the corresponding fission barriers in Figure 11. A typical example of such rearrangement is presented in Figure 6. The key point in this process is the transition from the first transitional state (the most right geometry in the first row) to the intermediate state (the most left figure in the second row). Exactly this transition results in significant lowering of the fission barrier, down to 0.34 eV from 0.48 eV in the situation when the atoms are continued to be pulled out from the cluster and the intermediate state is not allowed to form. The intermediate state is a super-molecule-like extended structure with a neck-like connection between its parts. The further fissioning of this intermediate structure is a simple stretching the neck and eventual complete separation of the fragments.

\(^{3}\) Melting temperature of bulk sodium is 371 K, while for clusters it was estimated to be about 300-400 K\(^{28,29}\).
TABLE III: Energies $E$ of the first several isomer states of $Na^{2+}_{10}$ cluster. Geometries of the isomers are shown in Figure 7. The calculations are done with the use of B3LYP exchange-correlation functional, molecular orbitals are expanded in 6-31G(d) basis. The energies are measured in atomic units, also differences with regard to the energy of the ground state (in eV) are given.

| Isomer’s nickname | Isomer’s symmetry group | Isomer’s energy $E$ | $E - E(T_d)$ |
|-------------------|-------------------------|---------------------|--------------|
| $T_d^{(1)}$       | $C_1$, distorted $T_d$  | -1622.6368          | 0.000        |
| iso1414x          | $C_4v$                  | -1622.6352          | 0.043        |
| $T_d^{(2)}$       | $C_1$, strongly distorted $T_d$ | -1622.6338 | 0.082        |
| iso145            | $C_1$                   | -1622.6338          | 0.082        |
| iso154            | $C_1$                   | -1622.6325          | 0.118        |

Let us now return to the first type of rearrangement. This type of rearrangement implies that there is a competition between one-step (“direct” fission) and two-step (fission via an intermediate isomer state) processes. Therefore, in order to make predictions concerning the fission activation energy and fission pathway for a given cluster isomer one has first to find energy barrier for the direct fission of the given isomer and then compare the height of this barrier with the heights of the barriers for transitions between given and several other low lying isomers, and also with the heights of the fission barriers of those isomers.

We present such analysis for the $Na^{2+}_{10}$ cluster. The energies of the several energetically favourable isomers are summarized in Table III their geometries are shown in Figure 7. The energy barrier heights for transitions between these isomers are presented in Table IV.

FIG. 7: (Color online) Four energetically favourable isomers of the $Na^{2+}_{10}$ cluster. A nickname for each of the isomers is given. The geometry of the ground state isomer $T_d^{(1)}$ is shown in Figure 3. Energies and symmetry groups of the isomers are summarized in Table III.

The analysis of the potential energy barriers for transitions between different isomer states of the $Na^{2+}_{10}$ cluster and of the potential energy barriers of fragmentation of the cluster leads to an interesting fact. It turns out that there are two fission pathways energetically equally probable in the symmetric fission of the $Na^{2+}_{10}$ cluster, $Na^{2+}_{10} \rightarrow 2Na^{+}_{5}$. Both of the pathways provide the minimum energy barrier (0.32 eV) for the symmetric fragmentation of the parent cluster. Both of the pathways involve rearrangement of the cluster’s structure. The energy barrier for the first pathway is shown in Figure 1. According to the first pathway, the fission starts from separating the two prospective fragments which later form a metastable super-molecule-like structure which leads to a well in the middle of the fission barrier.

4 Note, that the isomer with $C_4v$ group of symmetry presented here is different from the isomer shown in Figure 4 and discussed in the previous section.
TABLE IV: Energy barrier heights for transitions between the first several low-lying isomer states of Na$_{10}^{2+}$ cluster. The calculations are done with the use of B3LYP exchange-correlation functional, molecular orbitals are expanded in 6-31G(d) basis. The barrier heights are measured in eV.

| Initial isomer / Final isomer | $T_d^{(1)}$ | iso1414x | $T_d^{(2)}$ | iso145 | iso154 |
|-----------------------------|-------------|----------|-------------|--------|--------|
| $T_d^{(1)}$                  | –           | 0.12     | 0.092       | 0.11   | 0.13   |
| iso1414x                    | 0.08        | –        | 0.08        | 0.08   | 0.08   |
| $T_d^{(2)}$                  | 0.01        | 0.04     | –           | 0.017  | 0.04   |
| iso145                      | 0.03        | 0.04     | 0.017       | –      | 0.05   |
| iso154                      | 0.01        | 0.01     | 0.01        | 0.01   | –      |

The second fission pathway constitutes an even more complicated, two-stage process. On the first stage the base of the pyramid in the parent cluster $T_d^{(1)}$ reshapes from the triangle into a non-planar pentagon with an atom in its center forming a new isomer denoted $T_d^{(2)}$, Figure 7. After that the top four atoms in the pyramid and the atom from the center of the pentagon can be removed from the rest of the cluster. Again, this process proceeds via forming a necked-shaped super-molecule-like structure. For comparison, when the rearrangements are not allowed and the chosen group of atoms is simply pulled out of the parent cluster the lowest possible energy barrier (for removal the top four atoms and an atom from a vertex of the base triangle) equals to 0.63 eV.

The rearrangements of the cluster structure of the both types is a general feature of the metal cluster fission process. They occur for other clusters and fission channels too. As an illustration we plot in Figure 8 the fission barriers for fission of Na$_{18}^{2+}$ cluster in symmetric and dominant asymmetric channels. The geometries corresponding to different stages of the fission process in each channel are presented in Figure 9.

![FIG. 8: (Color online) Fission barriers for the symmetric (triangles), Na$_{18}^{2+}$ → 2Na$_9^+$, and dominant asymmetric (stars), Na$_{18}^{2+}$ → Na$_{15}^+$ + Na$_3^+$, channels for Na$_{18}^{2+}$ cluster, as functions of distance between the centers of mass of the fragments. Energy is measured from the energy of the ground $C_5$ state of the Na$_{18}^{2+}$ cluster. The geometries corresponding to different stages of the fission process in each channel are marked with subsequent numbers and depicted in Figure 9.](image_url)

To conclude, we have examined in detail fission of doubly charged sodium clusters Na$_{10}^{2+}$. Many new reference data are presented. Three main conclusions can be drawn from our studies. Firstly, geometry of the smaller fragment and geometry of its immediate neighborhood in the parent cluster (together with the electronic shell effects) play a leading role in defining the fission barrier height. Secondly, rearrangement of the cluster structure in the course of fission can lower the fission barriers significantly. We distinguish two general types of rearrangement: "necking" and fissioning via another low-lying isomer state of the parent cluster. And finally, accounting for geometrical structure of
the cluster leads to non-equivalence of different combinations of atoms in the cluster which in turn affects calculating the cluster’s entropy.

Acknowledgments

This work is supported by INTAS grant 03-51-6170 and by the Russian Foundation for Basic Research under the grant 03-02-18294-a. A.G.L. is grateful to the Alexander von Humboldt Foundation for financial support. We acknowledge an access to computer cluster at the Center for Scientific Computing of the Johann Wolfgang Goethe-University where the computations have been performed.

* Electronic address: oleg@mail.ioffe.ru
† On leave from: A.F. Ioffe Institute, Politechnicheskaja str. 26, St. Petersburg 194021, Russia; Electronic address: solovyov@ias.uni-frankfurt.de
1 J. P. Connerade and A. V. Solov’yov(eds.), Latest Advances in Atomic Clusters Collision: Fission, Fusion, Electron, Ion and Photon Impact, Proceedings of Europhysics Conference International Symposium "Atomic Cluster Collisions: fission, fusion, electron, ion and photon impact" (ISACC 2003), St. Petersburg, July 18-21, 2003 (Imperial College Press, London, 2004).
2 C. Guet, P. Hobza, F. Spiegelman and F. David (eds.), Atomic Clusters and Nanoparticles, NATO Advanced Study Institute, les Houches Session LXXIII, les Houches, 2000 (EDP Sciences and Springer Verlag, Berlin, 2001).
3 W. A. de Heer, Rev. Mod. Phys. 65, 611 (1993).
4 Lord Rayleigh, Philos. Mag. 14, 185 (1882).
5 P. Blaise, S. A. Blundell, C. Guet, and R. R. Zope, Phys. Rev. Lett. 87, 063401 (2001).
6 C. Bréchignac, Ph. Cahuzac, B. Concina, and J. Leygnier, Phys. Rev. Lett. 92, 083401 (2004).
7 C. Yannouleas, U. Landman, C. Bréchignac, Ph. Cahuzac, B. Concina, and J. Leygnier, Phys. Rev. Lett. 89, 173403 (2002).
8 X. Yang, X. B. Wang, S. Niu, C. J. Pickett, T. Ichiye, and L. S. Wang Phys. Rev. Lett. 89, 163401 (2002).
9 Y. Li, E. Blaisten-Barojas, D. A. Papaconstantopoulos, Phys. Rev. B 57, 15519 (1998).
10 F. Chandezon, C. Guet, B. A. Huber, D. Jalabert, M. Maurel, E. Monnand, C. Ristori, and J. C. Rocco, Phys. Rev. Lett. 74, 3784 (1995).
11 C. Bréchignac, H. Busch, Ph. Cahuzac, and J. Leygnier, J. Chem. Phys. 101, 6992 (1994).
12 A. G. Lyalin, O. I. Obolensky, A. V. Solov’yov, Il. A. Solov’yov, and W. Greiner J. Phys. B 37 L7 (2004).
13 B. Montag, P.G. Reinhard, Phys. Rev. B 52, 16365 (1995).
14 C. Bréchignac, Ph. Cahuzac, F. Carlier, M. de Frutos, R. N. Barnett, and U. Landman, Phys. Rev. Lett. 72, 1636 (1994).
R. N. Barnett, U. Landman, and G. Rajagopal, Phys. Rev. Lett. 67, 3058 (1991).

J. M. Eisenberg and W. Greiner, *Nuclear Theory. vol I. Collective and Particle Models* (North Holland, Amsterdam, 1985).

C. Bréchignac, Ph. Cahuzac, M. de Frutos, N. Kébalii, A. Sarfati, and V. Akulin, Phys. Rev. Lett. 77, 251 (1996).

C. Bréchignac, Ph. Cahuzac, N. Kébalii, and J. Leygnier, Phys. Rev. Lett. 81, 4612 (1998).

W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).

A. D. Becke, Phys. Rev. A 38, 3098 (1988).

A. D. Becke, J. Chem. Phys. 98, 5648 (1993).

C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B 37, 785 (1988).

I. A. Solov’yov, A. V. Solov’yov, and W. Greiner, Phys. Rev. A 65, 053203 (2002).

A. Lyalin, I. A. Solov’yov, A. V. Solov’yov, and W. Greiner, Phys. Rev. A 67, 063203 (2003).

J. B. Foresman and A. Frisch, *Exploring Chemistry with Electronic Structure Methods* (Gaussian Inc., Pittsburgh PA, 1996).

M. J. Frisch, *et al.*, Computer code GAUSSIAN 03, Rev. C.02 (Gaussian, Inc., Wallingford CT, 2004).

A. Lyalin, A. Solov’yov, and W. Greiner, Phys. Rev. A 65, 043202 (2002).

A. Rytkönen, H. Häkkinen, and M. Manninen, Phys. Rev. Lett. 80, 3940 (1998).

U. Röthlisberger and W. Andreoni, J. Chem. Phys. 94, 8129 (1991).