Stability and Observability of Charged Beryllium Clusters

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Electronic structure studies on neutral, singly and doubly charged Be_n clusters ($n \le 5$) have been carried out within the local spin-density formalism. We present results on their equilibrium geometries and atomization energies and discuss the stability of charged clusters. An extensive study of the Born-Oppenheimer surface of Be trimers is given and it is shown that small doubly charged clusters may exist in metastable states protected from dissociation by large energy barriers. The possibility of creating them by one- or two-step ionization processes critically depends on their geometries. We also address the issue of charge localization in doubly charged clusters.

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The study of charged clusters is of fundamental importance since cluster detection through mass spectrometry proceeds via ionization and detection of charged species. Singly ionized clusters of most elements are stable at low temperature; however, instability sets in when a cluster is multiply charged. The Coulomb repulsion between the charges acts against the cohesion and the clusters can spontaneously fragment even at low temperature. This phenomenon, called the "Coulomb explosion," has been of considerable experimental and theoretical interest. One of the central issues is the determination of the minimum or critical size, n_c, for which the multiply charged clusters are stable against the Coulomb repulsion.

For van der Waals clusters the experimental and theoretical situation[1] is reasonably clear; well-defined experimental values for n_c are known and simple theoretical models have been proposed. For metal clusters both the experimental and theoretical situations have yet to be clarified. Early experiments[2] had proposed the critical number $n_c = 31$ for doubly charged lead clusters, while in a recent experiment[3] doubly charged lead trimers have been observed. Several other[1] doubly charged dimers and trimers as well as small clusters[4] such as $\mathrm{Ag}_9{}^{++}$ have also been detected. Recently, $\mathrm{Hg}_5{}^{++}$ clusters ionized both by electron impact and single photon have been observed.[5]

Early theoretical explanations[6] admitted that the Coulomb explosion consists of the emission of charged single atoms from the surface of the cluster. They compared the change in Coulomb energy obtained by assuming the positive charges to be localized on opposite ends of the cluster with the binding energy per atom. Such models fail to explain the recent results on doubly charged clusters. Jellium models[7] taking only into account the initial-and final-state energies have also been proposed. Delley[8] was one of the first to suggest that the existence of a potential barrier is an important factor. Recent studies on doubly charged clusters[9] show that only a detailed study implying short-range forces and the existence of a potential barrier can explain the delicate balance between the cohesive and repulsive energies. Except for the work[10] on magnesium clusters ($n \le 5$) with a model potential, there is to our knowledge no systematic detailed study of the behavior of charged clusters.

In this Letter we present *ab initio* self-consistent local spin density (LSD) calculations on neutral, singly, and doubly charged beryllium clusters containing up to five atoms. The choice of beryllium, apart from its low number of electrons which render theoretical calculations easier, is motivated by the interest in group-II elements. These systems are well suited to study the evolution of bonding as a function of size: It is known that their dimers are weakly bounded molecules, while there is a reasonably strong metallic bonding in the bulk phase. Recent experiments[11] have studied this question for mercury clusters. However, in this work we shall mainly focus on doubly charged clusters. We have examined their equilibrium geometries, stability, the existence of potential barriers as well as the localization of the positive charge. We present in particular a detailed study of the $\mathrm{Be}_3{}^{++}$ Born-Oppenheimer (BO) surface and show that there is a metastable minimum with a high potential barrier, which makes its observation possible. The same situation holds for $\mathrm{Be}_4{}^{++}$, but for $\mathrm{Be}_5{}^{++}$ the linear chain is slightly bound. We also discuss the possibility of generating the doubly charged clusters using single or two-step ionization processes.

The theoretical studies were done with a program developed to study sodium clusters.[12] The molecular orbitals were represented[13] as a linear combination of Gaussian-type orbitals $(9s,3p)$, the calculations were carried out at the all-electron level, and the exchange-correlation contributions were treated within a LSD scheme. The molecular charge density and the exchange-correlation potential and energy were fitted by Gaussian functions centered on atomic sites and in between them. The Kohn-Sham equations are solved self-consistently to obtain the electronic states and energy. Our basis sets correctly reproduce the atomic ionization potentials and excitation energies to within 3% of the experimental values.

In Fig. 1 we show the minimum energy configurations of neutral, singly, and doubly ionized Be clusters containing up to five atoms, and in Table I the corresponding atomization energies are shown. The calculated equilibrium geometries of the neutral clusters are in good agreement with previous configuration-interaction calculations,[15] although the binding energies are large. The LSD approximation has been applied by Jones[16] to study the bonding properties of the neutral dimers of column-II elements. He shows that, although the dimer binding energies are too large, the basic physical picture and trends are correctly reproduced. A LSD calculation[17] of bulk Be reproduces the bulk cohesive energy within a few percent of the experimental value. This indicates that the LSD results will be better the larger the size of the clusters. It has been shown recently[18] that the overestimation of binding energy in the LSD scheme is related to the change in the nodal character of the orbitals, which is true in particular for the antibonding orbitals. We expect LSD to provide a better description for ionized clusters because of the removal of electrons from antibonding orbitals as well as their greater electron binding energies.

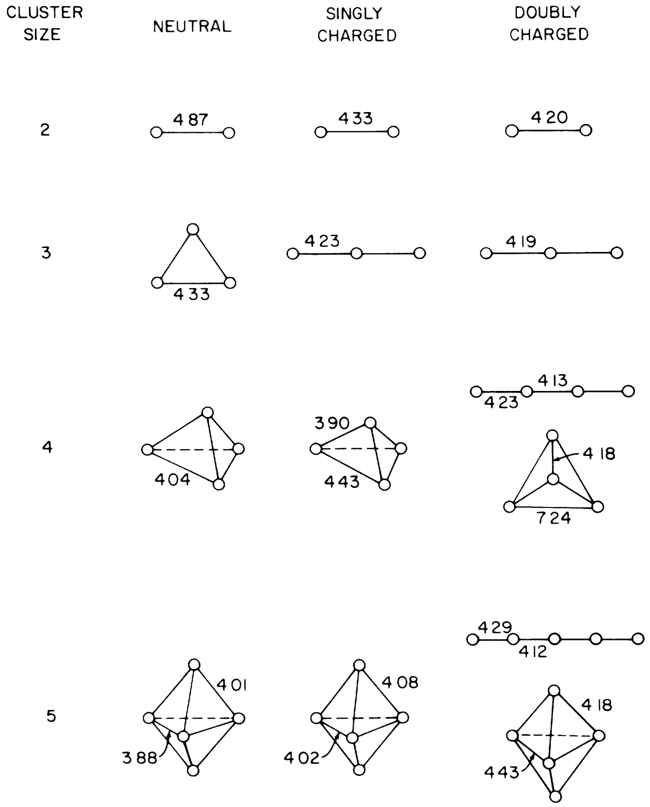

FIG. 1. Equilibrium configurations of neutral, singly, and doubly ionized Be clusters. Only lowest-energy configurations of neutral and singly charged clusters are shown.

Only the lowest-energy configuration for each singly ionized cluster size is reported in Fig. 1, although several other geometries have been considered. We find that for $Be_4{}^+$ the linear and rhombus geometries are only, respectively, 0.15 and 0.3 eV higher in energy than the tetrahedral one, the square and the centered triangle being higher. For $Be_5{}^+$ the linear chain is already 1.6 eV higher than the triangular bipyramid and the square pyramid is 0.5 eV higher. This shows that with increasing cluster size the three-dimensional behavior which maximizes the number of bonds becomes predominant.

The lowest-energy geometrical configurations of doubly ionized clusters $(n \leq 5)$ are linear chains as shown in Fig. 1. These structures, except for the barely stable $Be_5{}^{++}$. are not stable towards dissociation. They, however, all correspond to minima of the BO surface. In the case of the four- and five-atom particles, there are several other singlet geometries which are not much higher in energy. For $Be_4{}^{++}$ we find that the centered triangular geometry (see Fig. 1) is 0.5 eV higher and the rhombus is 1.2 eV higher than the linear chain. In the case of $Be_5{}^{++}$ the triangular bipyramid shown in Fig. 1 is 0.6 eV higher in energy than the linear chain. We also find that the energies of the square pyramid, the centered tetrahedra, the centered rhombus, and the regular pentagon are, respectively, 0.8, 0.9, 2.1, and 2.5 eV higher than the linear chain. For $Be_5{}^{++}$ it appears that, apart from the linear chain, the structures which have the largest number of nearest neighbors have the lowest energy. The equilibrium geometry corresponds to a delicate balance between the attractive bonding energy which increases with the number of nearest neighbors and the repulsive Coulomb energy, which is minimized in the

TABLE I. Atomization energies (electronvolts) of neutral and charged Be clusters for the lowest-energy equilibrium configurations. The numbers in parentheses correspond to experimental values (Ref. 14).

n	Be_n	$Be_n{}^+$	$Be_n{}^{++}$
2	0.36 (0.11)	2.19	−2.57
3	1.60	3.91	1.28
4	4.34	5.61	4.00
5	6.09	8.45	6.37

linear chain. We expect that when the cluster size grows, the three-dimensional structures will stabilize, although this is for larger cluster sizes than in the singly ionized case.

An analysis of the hole charge density shows that the naive picture in which all missing charges are localized at the ends of the chain is too simple. We give in Fig. 2 the linear chain electronic charge density from which we have subtracted the charge density obtained by superposition of neutral atoms. We estimate that the positive charge at the end of the linear chain corresponds to 0.5 missing electron; each torus-shaped charge depletion around inner atoms corresponds to $\frac{1}{3}$ or more electronic charge. A comparison between the charge densities for the neutral, singly, and doubly ionized triangular bipyramids shows a similar behavior. Some of the holes are localized at the two outermost atoms of the bipyramid, but there are also holes localized at the exterior of the other three atoms. Everything happens as if the charged clusters behave as a metal in distributing the positive charges outside the cluster.

The doubly charged clusters ($n \leq 5$) are not or are barely stable towards dissociation; they are, however, metastable and protected from dissociation by energy barriers for times long compared with the typical 10-μs observation time. For transition-metal dimers[9] it has been shown that the potential barrier results from the interplay between the increasing attractive bonding strength and increasing repulsive Coulomb interaction when the interatomic distance decreases. In the case of column-II elements, the stabilizing energy of the bond is particularly important, since for doubly charged dimers the electrons are taken out of the antibonding orbitals. Our calculations for Be_2^{++} give an energy barrier of 0.9 eV compared with 1.3 eV in configuration interaction.[19] For Be_3^{++} we have done an extensive study of the BO surface in calculating 140 points for angles between 0° and 120° and interatomic distances R and S between 3.4 and 9 a.u. The minimum-energy configuration corresponds to the linear chain given in Fig. 1, and the lowest-energy dissociation path corresponds to the separation of a Be^+ atom from a charged dimer, whose interatomic distance, as expected, gradually changes from the trimer to the singly charged dimer distance. The minimum height of the potential barrier is equal to 1.4 eV and a simple WKB approximation shows that the lifetime at low temperature is much longer than the observation time. In principle, Be_3^{++} is thus observable, if we assume that it can be created in the potential well.

In order to more closely study this question we give in

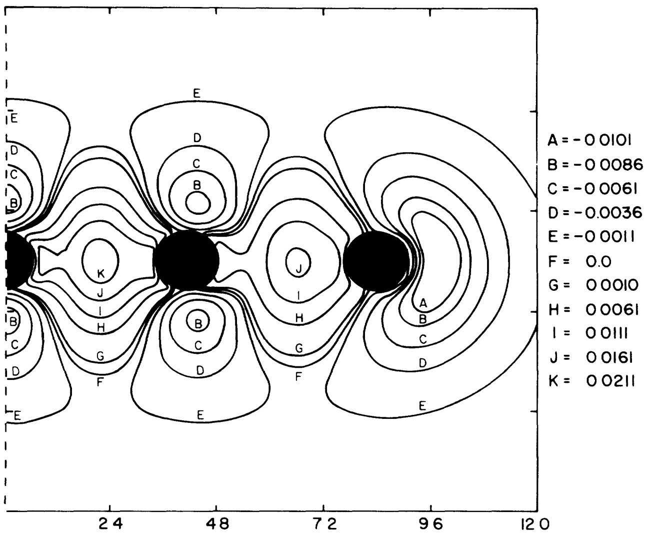

FIG. 2. Difference charge density (atomic units) representing the difference between the electronic charge density in Be_5 minus the charge density obtained by superposition of neutral Be atoms at the Be sites in Be_5^{++}.

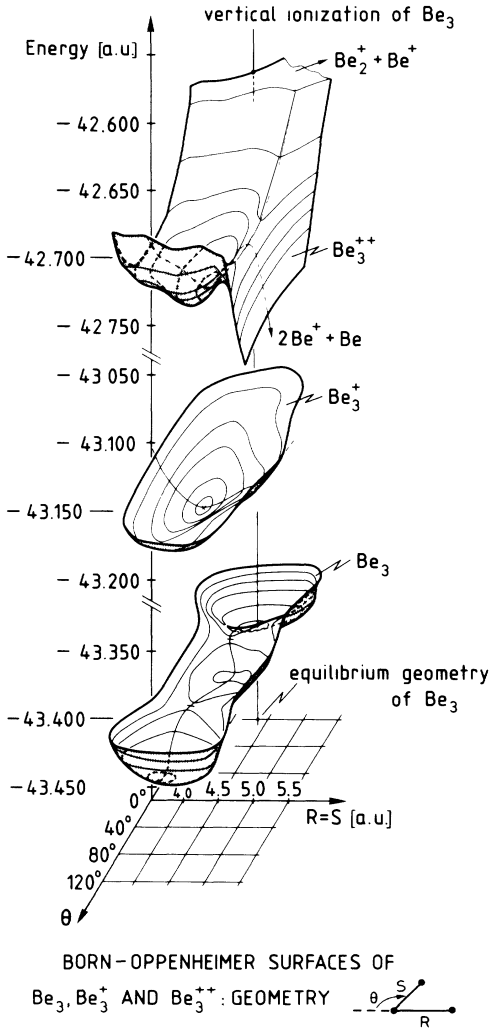

FIG. 3. Born-Oppenheimer surface of singly and doubly ionized and neutral Be_3 corresponding to various isosceles triangular configurations.

Fig. 3 a representation of the BO surface of Be_3, $Be_3{}^+$, and $Be_3{}^{++}$ for the isosceles triangle geometry. This exact drawing clearly shows that in a single-step double-ionization process there is no chance that a metastable isolated $Be_3{}^{++}$ cluster can be formed. Even if the ionizing energy is equal to the vertical double-ionization potential the cluster will reach an energy higher than its dissociation threshold. The coupling between the electronic and vibronic degrees of freedom will "heat" the cluster which will then quickly dissociate. It is only if there are effective ways of cooling the cluster more quickly than it dissociates, by collision for example, that a small probability of our observing it may exist. In a two-step process, if sufficient time is given to the singly ionized cluster to reach its equilibrium geometry, a subsequent ionization is possible since the equilibrium geometries of the singly and doubly ionized trimers are similar.

Such a detailed analysis is difficult to make in the case of $Be_4{}^{++}$ and $Be_5{}^{++}$. The lowest dissociation path for the linear equilibrium geometry of $Be_4{}^{++}$ corresponds to fragmentation into two singly charged dimers, whose final energy is lower by 0.3 eV. The linear chain $Be_5{}^{++}$ dissociates into a charged trimer and a charged dimer higher in energy by 0.2 eV. In both cases we expect that a potential barrier of the order of 1 eV will prevent dissociation. However, for reasons similar to the trimer case, it seems unlikely that the doubly charged linear equilibrium geometries can be reached in a single-ionization process. A single-step double-ionization process is possible for $Be_5{}^{++}$ if we admit that the final geometry corresponds to the triangular bipyramid. In this case the lowest dissociation path compatible with the geometrical structure corresponds to the dissociation of $Be_5{}^{++}$ into tetrahedral $Be_4{}^+$ and a singly charged atom, which is 0.75 eV higher in energy than the bipyramidal $Be_5{}^{++}$. These considerations could explain the observation of $Hg_5{}^{++}$ clusters, while $Hg_3{}^{++}$ is not observed.

To sum up, we have shown that the observability of small doubly charged clusters critically depends on the existence of potential barriers and on the relative equilibrium geometries of the neutral, singly, and doubly ionized clusters. For larger sizes we expect that neutral and charged clusters will be three dimensional and that doubly charged clusters will be stable. The requirements to create and observe them will thus be less severe. It is not clear at this stage that the behavior calculated for Be clusters is representative of all column-II elements, since it is known that the binding energy per bond of the neutral beryllium clusters converges quickly towards the bulk value. Calculations on magnesium clusters are under way to clarify this point.

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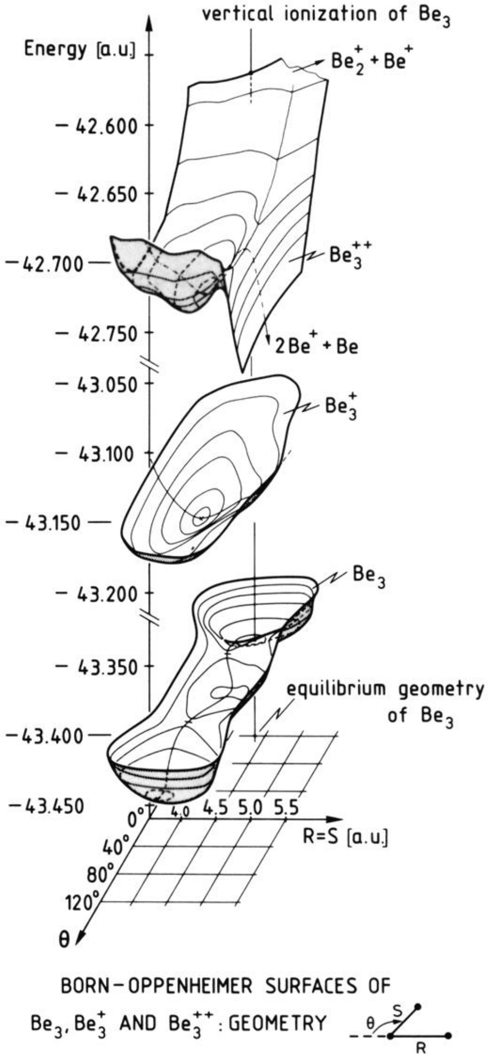

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