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Experimental dissociation energies of metal cluster dications and their interpretation in a liquid-drop model with empirical corrections

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The dissociation energies of doubly charged silver cluster ions in the size range $9 \leqslant n \leqslant 25$ are measured by multiple collision induced dissociation. They are compared to the dissociation energies of singly charged clusters. To this end, the latter are used to calculate shell corrections in a macroscopic-microscopic model. Good agreement between the resulting predictions of the dissociation energies of the doubly charged systems and the experimental values is found, which indicates the strong influence of electronic effects on the stability of small silver clusters. [S1050-2947(99)05808-4]

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I. INTRODUCTION

One of the central issues of metal cluster research [1,2] is the question to what extend the geometric and the electronic structure control the clusters' properties. Experimentally, such information can be obtained by measuring a property over a broad range of cluster sizes and over several charge states. The latter aspect was first observed in the investigation of abundance spectra of singly charged noble metal cluster anions and cations M_n^z $(z=\pm 1)$ [3]: Shell closures and the odd-even-effect were found to be mainly a function of the number of atomic valence electrons, i.e., $n_e = n - z$ for the case of the monovalent Ib metals. As far as dissociation energies are concerned, most experimental investigations have been performed with singly charged cluster cations. The present investigation is an extension of such measurements to doubly charged clusters.

Doubly charged clusters, especially metal clusters, have found continuous interest over the past decade [4,5]. Again, the initial information came from abundance spectra. Appearance sizes for doubly charged systems, depending on the production mechanisms were observed, e.g., for silver $n=9$ [6] or $n=15$ [7]. In addition electronic shell closures and the odd-even effect were reproduced at higher charge states [8,7]. Later experiments yielded information on the decay pathways. In general, for large systems neutral atom evaporation has been observed, while smaller clusters undergo charge-symmetric, mass-asymmetric fission, i.e., decay into two charged fragments. This behavior, which is expected by basic considerations such as, e.g., in a liquid-drop model [9], was first found for alkali-metal clusters [10] and gold clusters [9]. The latter results were confirmed by Penning-trap experiments [11,12] and extended to other metals [13], in particular to silver [14]. The dominant fragmentation pathways of Ag_n^{2+} are neutral momomer evaporation for $n > 16$ and trimeric fission for most clusters with $n \leqslant 16$. Exceptions from the rule are Ag_{11}^{2+} and Ag_{15}^{2+} which undergo monomer evaporation [14]. Thus, they indicate the influence of microscopic structure.

Apart from the kinetic energy release study of Li_{26}^{2+} by Bréchignac *et al.* [15], little is known so far about the dissociation energies of doubly charged metal clusters, i.e., in the case of neutral monomer evaporation the energy required for the separation of a neutral atom and in the case of fission the energy required for the decay into two charged particles (the fission barrier). Recently the method of multiple collision induced dissociation (MCID) in a Penning trap for the determination of dissociation energies, originally employed for multiply charged gold clusters [16], was presented in detail for the case of singly charged silver clusters [17]. The present investigation is an extension to doubly charged silver clusters. The differences in the dissociation energies of the two charge states can partly be understood in the liquid-drop model. We present a macroscopic-microscopic model, where the experimental results from singly charged silver clusters are used to deduce empirical corrections with respect to the liquid-drop model. These corrections are subsequently employed for predictions of the dissociation energies of doubly charged clusters. The procedure of adding (experimental or theoretical) microscopic corrections to a macroscopic model is a well known method in the field of nuclear physics [18,19] and cluster physics (see, e.g., Refs. [20,21]). In the field of doubly charged clusters, it has been used to estimate fission barriers of doubly charged systems [22–25,20,5]. However, up to now no experimental data has been available for a direct comparison of the two charge states. We have performed measurements of the dissociation energies of Ag_n^{+}, $n=2-25$ and Ag_n^{2+}, $n=9-25$ and are thus able to check the influence of electronic and geometric structure on the clusters' stability.

The outline of this paper is as follows. The experimental setup and the MCID method are briefly described in Sec. II.

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Subsequently, the results for doubly charged silver clusters, an overview of which has already been presented [26], are discussed in detail and they are compared to previous results for singly charged silver clusters [17] (Sec. III A). The results are then combined for the extension of the macroscopic liquid drop model (Sec. III B) by use of empirical corrections as the microscopic contributions of a macroscopic-microscopic model (Sec. III C).

II. EXPERIMENTAL SETUP AND PROCEDURE

The experiments have been performed at the Mainz Cluster Trap, a Penning-trap system that has been described recently [27–29]. MCID as used for the determination of fragmentation pathways of singly and doubly charged silver clusters is described in detail in Refs. [30] and [14]. For the case of Ag_n^{2+}, in a first step singly charged metal cluster ions are produced by a laser vaporization source and transferred into a hyperbolic Penning trap. Then mass selective quadrupolar cooling [31] is applied to accumulate and center the externally created clusters in the trap. The clusters are subsequently bombarded for 600 ms with 150-eV electrons. Thus the clusters may be further ionized [11,32,33], in the present case to charge state $z=2$. Next, an ion ensemble of a specific cluster size-over-charge ratio n/z is selected by radial ejection of all other ions. For MCID the cyclotron motion of the cluster ions is excited by a 1-ms resonant excitation and an argon gas pulse is directed into the trap volume. A storage period of 270 ms allows the clusters to collide with the argon atoms and to decay to smaller cluster sizes. The charged reaction products remain stored in the trap until the surviving precursors and the fragment ions are axially ejected and analyzed by time-of-flight (TOF) mass spectrometry. Single ion detection is performed by use of a conversion dynode detector. Typically an experimental cycle leads to 25 detected ions. To increase the statistical significance of the data the cycle is repeated 50 times for a given set of experimental parameters.

For the determination of dissociation energies the fragment ion yield is measured as a function of the initial kinetic energy of the cluster ensemble. The data analysis includes two main steps: (1) An evaluation as to which fraction of the kinetic energy E_{kin} is converted in the collisional process to excitation energy E_{exc} of the clusters and (2) a decay model to describe the relation between this excitation energy, the dissociation energy, and the fragment yield at a given time after excitation. A detailed description of the data analysis is given in Ref. [17], where it is applied to the dissociation energies of singly charged silver clusters Ag_n^+ $(n=2-25)$.

III. RESULTS AND DISCUSSION

A. Experimental results

The experimental results of MCID of silver clusters are summarized in Fig. 1. The top part shows the dissociation energies of doubly charged clusters Ag_n^{2+} [26] (the values are found in Table I); the bottom part gives the dissociation energy of the singly charged clusters Ag_n^+ [17]. The measurements have been performed from the smallest cluster available, i.e., from Ag_2^+ and Ag_9^{2+} (due to insufficient intensity at lower cluster sizes) up to Ag_{25}^+ and Ag_{25}^{2+}, i.e., well above the electronic shell closure that is expected at $n_e=n-z=20$ (see below), where z denotes the clusters charge state (silver is a monovalent element).

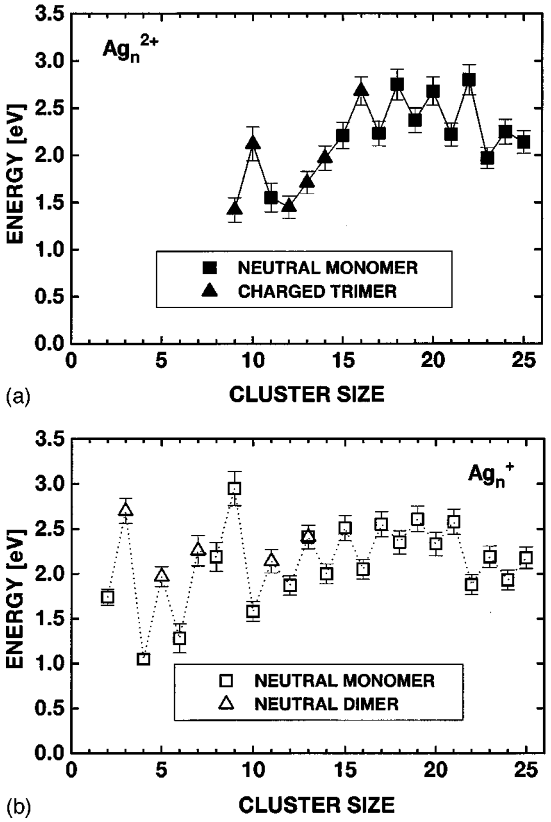

FIG. 1. Top: dissociation energies of doubly charged silver clusters Ag_n^{2+}, $n=9–25$ [26]. Bottom: dissociation energies of singly charged silver clusters Ag_n^+, $n=2-25$ [17].

TABLE I. Dissociation energies of doubly charged silver clusters Ag_n^{2+} $(9\leqslant n\leqslant 25)$.

n	$E_0\pm\sigma$ (eV)
9	1.42±0.13
10	2.12±0.18
11	1.55±0.15
12	1.45±0.12
13	1.71±0.12
14	1.97±0.13
15	2.21±0.14
16	2.68±0.15
17	2.23±0.13
18	2.75±0.16
19	2.37±0.13
20	2.68±0.15
21	2.22±0.12
22	2.80±0.16
23	1.97±0.11
24	2.25±0.13
25	2.14±0.12

As mentioned above, there are two competing decay pathways in the case of Ag_n^{2+} [14], the evaporation of neutral atoms $Ag_n^{2+}\rightarrow Ag_{n-1}^{2+}+Ag$, and the charge symmetric, but mass-asymmetric fission into a charged trimer and the corresponding fission product $\mathrm{Ag}_n{}^{2+} \rightarrow \mathrm{Ag}_{n-3}{}^{+} + \mathrm{Ag}_3{}^{+}$. The main decay pathway of doubly charged silver clusters of size $n \leqslant 16$ is fission, with the exceptions of $\mathrm{Ag}_{11}{}^{2+}$ and $\mathrm{Ag}_{15}{}^{2+}$. The latter as well as larger clusters, $n \geqslant 17$, preferentially undergo neutral monomer evaporation. The clusters of size $n=18$, which preferentially decay by neutral monomer evaporation, also show some contribution from trimer fission. Previous sputter experiments [34] that seemed to indicate mass-symmetric fission processes have thus been reinterpreted in terms of sequential decays [14].

For the dissociation energies of doubly charged silver clusters (top of Fig. 1, Table I), several features are observed: (1) Clusters with $n \geqslant 16$ show an odd-even staggering: the even-size clusters are more stable than their odd-size neighbors. (2) Below $n=16$ this staggering vanishes for the fissioning clusters $n=12-16$. (3) Cluster sizes of outstanding stability are $\mathrm{Ag}_{10}{}^{2+}$ and $\mathrm{Ag}_{22}{}^{2+}$.

For singly charged silver clusters (bottom of Fig. 1), the dissociation energies show two main features. (1) There is an odd-even staggering with odd-size clusters having a higher stability than even-size clusters. (2) The cluster sizes $n=3$, 9, and 21 have an outstandingly high dissociation energy, especially in comparison to the next larger neighbor. While larger clusters decay by evaporation of a neutral atom, some odd-size clusters ($n=3,5,7,11$) emit a dimer [30].

From these observations it is concluded that the main phenomena are a function of the number of atomic valence electrons $n_e = n - z$. To better illustrate this feature, the dissociation energies and two derived quantities are plotted as a function of n_e in Fig. 2. To follow the trend of the dissociation energies without the odd-even staggering, the mean of dissociation energies of neighboring cluster sizes is taken (middle part of Fig. 2):

$$\overline{D}(n_e) = \frac{1}{2}[D(n_e) + D(n_e+1)]. \tag{1}$$

To segregate the odd-even effect, the difference between the dissociation energy of a cluster with size n and the mean of the dissociation energies of the neighboring clusters $n-1$ and $n+1$ is calculated:

$$\Delta^{oe}(n_e) = D(n_e) - \frac{1}{2}[D(n_e+1) + D(n_e-1)]. \tag{2}$$

This term, which is proportional to the second derivative of the dissociation energies may be dubbed ''odd-even energy'' and is displayed in the bottom part of Fig. 2. In the range $n_e = 13-23$ the odd-even effect has about the same amplitude for both charge states, while it vanishes for the fissioning doubly charged clusters below $n_e = 14$. The shell effect at $n_e = 20$ has the same magnitude for singly and doubly charged clusters. The dissociation energies of small doubly charged systems are substantially smaller than those of singly charged clusters: This difference is as large as 1 eV for $n_e = 7,8$, thus demonstrating the destabilizing influence of the second charge. The structures of neighbor-averaged dissociation energies can be understood qualitatively as shell closures ($n_e = 8,20$) in a spherical jellium model [1,2] and the odd-even staggering may be interpreted in terms of the Jahn-Teller effect [35]. There are no signs for geometric effects, i.e., effects depending only on the number of constitutent atoms, as would be, e.g., an atomic shell at $n=13$ [36].

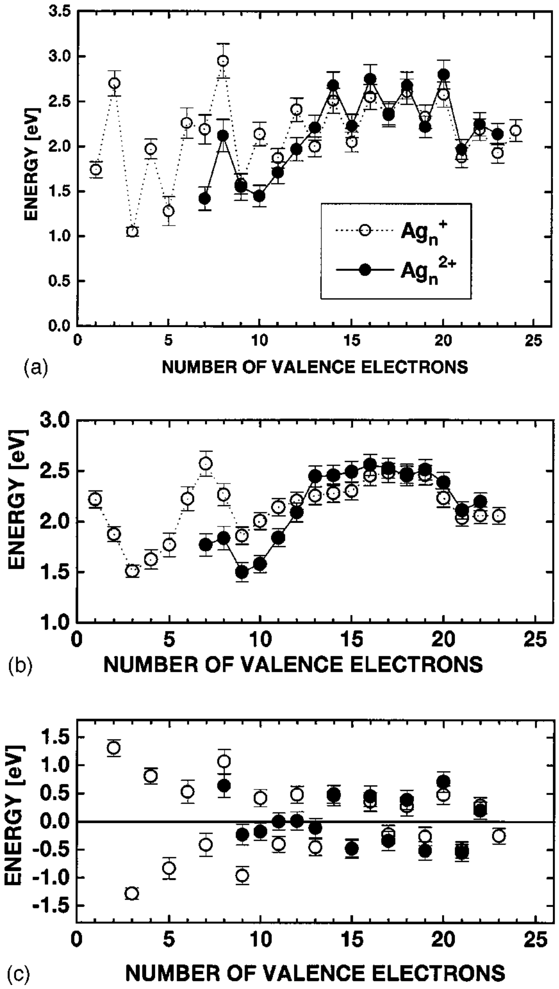

FIG. 2. Comparison of singly and doubly charged silver clusters as a function of the number of valence electrons $n_e = n - z$. Top: dissociation energies. Middle: mean of the dissociation energies of neighboring cluster sizes [Eq. (1)]. Bottom: odd-even energy [Eq. (2)].

The electronic features of noble metal clusters as a function of charge state have been observed qualitatively in abundance spectra: by Katakuse *et al.* for singly charged anions and cations [3] and for doubly and triply charged silver clusters by Rabin *et al.* [37] and Kandler *et al.* [7] as well as recently at the Mainz cluster trap in the cases of silver and gold [33,38]. Given the close similarity of the dissociation energies of the larger $\mathrm{Ag}_n{}^{+}$ and $\mathrm{Ag}_n{}^{2+}$ clusters, a quantitative comparison over the whole size range of the present measurements has been performed by the following procedure: The deviations of the dissociation energies of $\mathrm{Ag}_n{}^{+}$ from the prediction of the liquid-drop model have been determined as a function of cluster size. These results have been used for the prediction of the corresponding deviations for $\mathrm{Ag}_n{}^{2+}$ and compared to the experimental values. Section III B gives a brief account of the liquid-drop model. The comparison is performed in Sec. III C.

B. Macroscopic model

For the theoretical description of the energetics of metal clusters, the liquid-drop model is used as a first-order ap-

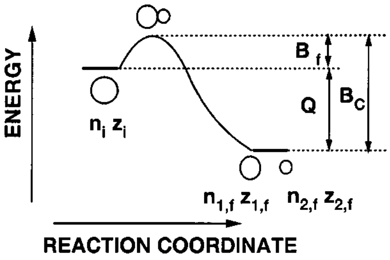

FIG. 3. Fission barrier in the touching sphere model. For details see text.

proach. The total binding energy of a metal cluster is estimated as the sum of a volume, surface, and Coulomb term [9]:

$$E_{\mathrm{LD}}(n,z)=a_v n-a_s n^{2/3}-z^2 a_c n^{-1/3}. \tag{3}$$

In this contribution, the parameters a_v, a_s, and a_c are derived from macroscopic (bulk) properties at the melting point. The volume parameter is calculated following the procedure suggested by Näher *et al.* [5] as $a_v=2.69$ eV [39]. The Coulomb parameter $a_c=4.34$ eV is calculated from the constituent radius $r_0=1.66\times10^{-10}$ m [40]:

$$a_c=\frac{e^2}{2\times4\pi\epsilon_0\times r_0}. \tag{4}$$

The surface parameter a_s can be correlated to the surface tension

$$a_s=4\pi r_0^2\sigma. \tag{5}$$

With $\sigma=0.934$ J/m^2 [40] one obtains $a_s=2.02$ eV. The difference in the total energy of the initial state (n_i,z_i) and the final state (two fragments with $n_{1,f},z_{1,f}$ and $n_{2,f},z_{2,f}$) gives the Q value of the decay

$$Q^{\mathrm{LD}}(n_i,z_i;n_{1,f},z_{1,f})=E_{\mathrm{LD},i}-E_{\mathrm{LD},f}. \tag{6}$$

With this definition, $Q>0$ signifies an endothermic and $Q<0$ an exothermic process. In the case of neutral monomer evaporation the derivative of Eq. (3) results in

$$\begin{aligned}Q^{\mathrm{LD}}(n,z;n-1,z)&=\frac{\partial E_{\mathrm{LD}}(n,z)}{\partial n}\\&=a_v-\frac{2}{3}a_s n^{-1/3}+\frac{1}{3}z^2 a_c n^{-4/3}.\end{aligned} \tag{7}$$

As proposed in Ref. [5] the fission process may be described within the touching sphere model. It is schematically visualized in Fig. 3. The fission barrier B_f is given by the Coulomb interaction of two touching spheres (i.e., the fragments) and the Q value of the fragmentation

$$B_f=B_c+Q. \tag{8}$$

(Note that in our definition $Q<0$.) This approach is valid for the situation shown in Fig. 3 in the limit of low fissilities x:

$$x(n,z)=\frac{a_c}{2a_s}\frac{z^2}{n}. \tag{9}$$

In the case of doubly charged silver clusters, the fissilities fall in the range of $x=0.17$ $(n=25)$ to $x=0.48$ $(n=9)$.

For the Coulomb interaction between the two cluster fragments their polarizabilities has to be taken into account. The potential energy between two polarizable particles can be calculated numerically with image charges in an iterative procedure [5]. An equally good but much simpler approach is the use of the analytical expression developed in Ref. [41] for the interaction between charges z_1,z_2 with polarizabilities α_1,α_2 at a distance s:

$$E_{1,2}^{\mathrm{pol}}(s)=\frac{A_2}{A_4}\frac{z_1z_2e^2}{4\pi\epsilon_0 s}-\frac{\alpha_1}{2s^3}\frac{1}{A_4}\frac{z_2^2e^2}{4\pi\epsilon_0 s}-\frac{\alpha_2}{2s^3}\frac{1}{A_4}\frac{z_1^2e^2}{4\pi\epsilon_0 s}. \tag{10}$$

Here A_n is given as

$$A_n=1-\frac{n\alpha_1\alpha_2}{s^6}. \tag{11}$$

The polarizability of a conducting sphere, i.e., the metal cluster, is simply [41]

$$\alpha=R^3=r_0^3 n. \tag{12}$$

The fission barriers for the decay of doubly charged silver clusters into two singly charged fragments for all possible mass asymmetries are shown in Fig. 4 (top) for the cluster sizes $n=9$, 18, 25. For larger clusters $(n=18,\ 25)$, highly mass-asymmetric fission is preferred, while for smaller systems $(n=9)$ more mass-symmetric channels should be favored. Experimentally only trimer fission is observed which competes with neutral monomer evaporation. The corresponding dissociation energies are shown in Fig. 4 (bottom). In accordance to the experimental results, fission is expected only for clusters below $n=14$. Thus the critical size and the general mass-asymmetry of the fission are predicted very well by the liquid-drop model. The assumption of trimeric fission had to be put in by hand at this stage. However, it can be seen in Fig. 1 that $\mathrm{Ag}_3{}^+$ has a large binding energy and therefore, trimer fission can be expected to be the most probable mass-asymmetric fission process. The next subsection gives further examples on how microscopic aspects influence the dissociation pathways.

C. Empirical microscopic corrections

The macroscopic liquid-drop model cannot account for the additional structure observed in the dissociation energies as a function of cluster size, i.e., the odd-even staggering and the shell closures. In the following we present a macroscopic-microscopic model for the prediction of dissociation energies, in the present case for doubly charged silver clusters. The difference in the *measured* dissociation energies of *singly* charged clusters and the liquid-drop model are considered to be due to the microscopic cluster structure. Thus *microscopic corrections* can be deduced. These values are added to the predictions of the liquid-drop model for the corresponding *doubly* charged clusters.

In general, we denote with $D(n^{z+},m^{p+})$ the dissociation energy of a cluster Ag_n^{z+} into the fragments Ag_m^{p+} and

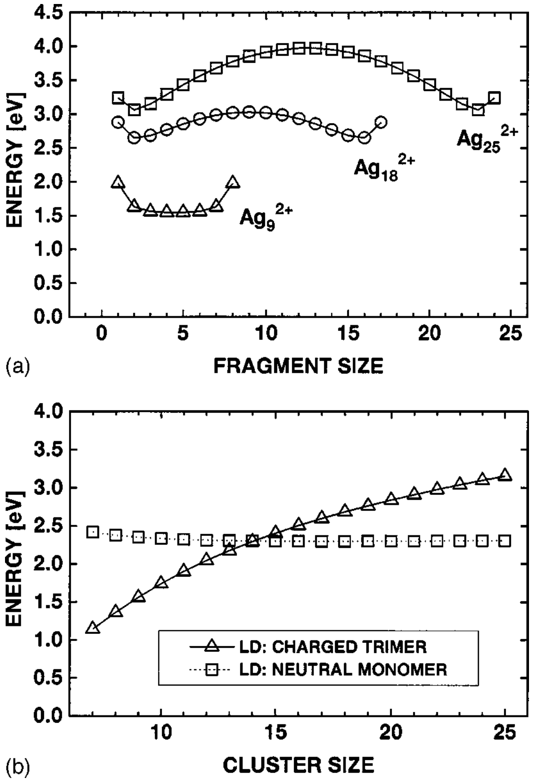

FIG. 4. Fission barriers for the decay of doubly charged silver clusters into two singly charged fragments in the touching sphere model. Top: for all fission pathways of $\mathrm{Ag}_{25}{}^{2+}$ ($x=0.17$), $\mathrm{Ag}_{18}{}^{2+}$ ($x=0.24$), and $\mathrm{Ag}_{9}{}^{2+}$ ($x=0.48$). Bottom: fission barriers for trimer fission and the dissociation energies for neutral monomer evaporation as a function of cluster size.

$\mathrm{Ag}_{n-m}^{(z-p)+}$. For the evaporation of a neutral monomer from the cluster $\mathrm{Ag}_n{}^+$, the measured dissociation energy $D(n^+,1^0)$ and the liquid-drop prediction $D^{\mathrm{LD}}(n^+,1^0)=E_f^{\mathrm{LD}}-E_i^{\mathrm{LD}}=-Q^{\mathrm{LD}}(n,1;n-1,1)$ can be related through the correction of the initial state, $E^{\mathrm{mic}}(n^+)$, and the final state, $E^{\mathrm{mic}}((n-1)^+)$. The correction of the second fragment, the neutral monomer, is set to zero: $E^{\mathrm{mic}}(1^0)=0$. Hence,

$$D(n^+,1^0)=(E_f^{\mathrm{LD}}-E_f^{\mathrm{mic}})-(E_i^{\mathrm{LD}}-E_i^{\mathrm{mic}}) \tag{13}$$

or

$$D(n^+,1^0)=D^{\mathrm{LD}}(n^+,1^0)-E^{\mathrm{mic}}(n^+)+E^{\mathrm{mic}}((n-1)^+). \tag{14}$$

We start with the trimer's correction $E^{\mathrm{mic}}(3^+)$ which is the only free fit parameter. The following corrections $E^{\mathrm{mic}}((n>3)^+)$ are obtained by subsequent application of Eq. (13):

$$E^{\mathrm{mic}}(n^+)=E^{\mathrm{mic}}(3^+)+\sum_{m=4}^{n}[D^{\mathrm{LD}}(m^+,1^0)-D(m^+,1^0)]. \tag{15}$$

As noted above, some small odd-size clusters decay by dimer instead of monomer evaporation. For the present investigation these cases are not distinguished and treated as if it was monomer evaporation. Under these assumptions the corrections $E^{\mathrm{mic}}(n=3^+-25^+)$ are calculated and used to predict the dissociation energies of doubly charged clusters. To this end it is further assumed that the corrections depend only on the number of atomic valence electrons, i.e.,

$$E^{\mathrm{mic}}(n^{2+})=E^{\mathrm{mic}}((n-1)^+). \tag{16}$$

Thus the expected dissociation energy for monomer evaporation of doubly charged clusters is given by

$$D(n^{2+},1^0)=D^{\mathrm{LD}}(n^{2+},1^0)-E^{\mathrm{mic}}(n^{2+})+E^{\mathrm{mic}}((n-1)^{2+}) \tag{17}$$

$$=D^{\mathrm{LD}}(n^{2+},1^0)-E^{\mathrm{mic}}((n-1)^+)+E^{\mathrm{mic}}((n-2)^+). \tag{18}$$

This procedure can by applied in an analogous way to trimer fission, where $D(n^{2+},3^+)$ denotes the fission barrier

$$D(n^{2+},3^+)=D^{\mathrm{LD}}(n^{2+},3^+)-E^{\mathrm{mic}}(n^{2+})+E^{\mathrm{mic}}((n-3)^+)+E^{\mathrm{mic}}(3^+) \tag{19}$$

$$=D^{\mathrm{LD}}(n^{2+},3^+)-E^{\mathrm{mic}}((n-1)^+)+E^{\mathrm{mic}}((n-3)^+)+E^{\mathrm{mic}}(3^+). \tag{20}$$

These equations are applied to the fission barriers and dissociation energies of Fig. 4; the results are shown in Fig. 5. The fission barriers (top) still show a preference for highly mass-asymmetric fission. This holds even for the decay of $\mathrm{Ag}_{18}{}^{2+}$, where the mass-symmetric fission into two closed-shell $\mathrm{Ag}_9{}^+$ clusters also shows some energetic preference with respect to small mass asymmetries, however, not with respect to trimer fission.

A comparison between the expectations for neutral monomer evaporation and trimer fission is shown in Fig. 5 (bottom). The values for monomer evaporation reflect the measured dissociation energies of singly charged clusters, with the shell and odd-even effect shifted by one unit in cluster size. In contrast, the fission barriers show no odd-even staggering: The microscopic corrections of initial and final states nearly cancel out (the initial cluster and the main fragment are both either odd- or even-n_e systems) and only shell effects remain. The absolute values of the fission barriers depend on the trimers' shell correction $E^{\mathrm{mic}}(3^+)$ which gives a general offset to the dissociation energies and which is, as mentioned above, a free parameter. It has been set to a value of $E^{\mathrm{mic}}(3^+)=-0.25$ eV, as this leads to the correct prediction of all observed dissociation pathways: Not only the trend from monomer evaporation to trimer fission for smaller clusters, but also the exceptional monomer evaporation for $\mathrm{Ag}_{11}{}^{2+}$ and $\mathrm{Ag}_{15}{}^{2+}$ as well as the observed competition between the two fragmentation pathways of $\mathrm{Ag}_{18}{}^{2+}$ are reproduced.

In Fig. 6 the predictions of the macroscopic-microscopic model are compared to the measured dissociation energies of doubly charged clusters for the low energy decay pathways. The agreement is remarkable, considering the simplicity of the models involved.

As noted above the method presented requires several assumptions and hence its application is limited. For example, the liquid-drop model is based on the derivation of the parameter set (a_v, a_s, a_c) from the elements' bulk proper-

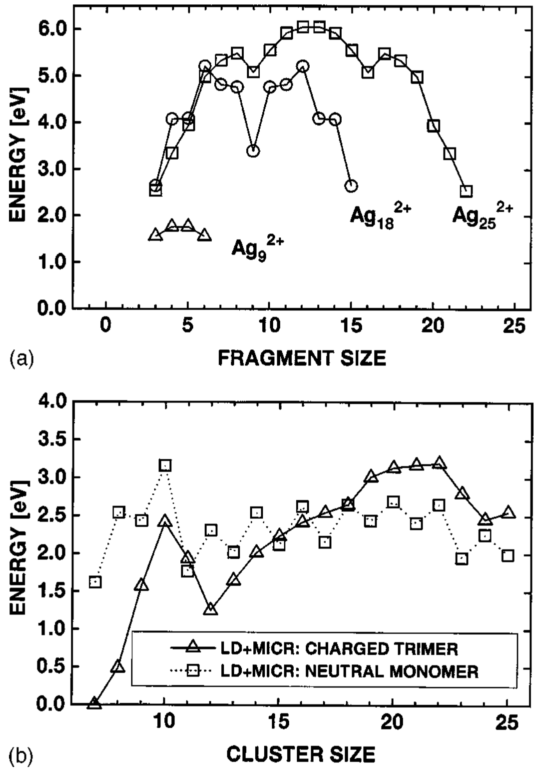

FIG. 5. Fission barriers for the decay of doubly charged silver clusters into two singly charged fragments in the touching sphere model with empirical shell corrections, Eq. (20). Top: for the different fission channels of $\mathrm{Ag}_{25}{}^{2+}$, $\mathrm{Ag}_{18}{}^{2+}$, and $\mathrm{Ag}_{9}{}^{2+}$. Bottom: fission barriers for trimer fission and the dissociation energies for monomer evaporation, Eq. (18).

ties, and a choice of the temperature has to be made. (In the present contribution the procedures of Näher *et al.* [5] are followed.) The complexity of the fission process is simplified by the application of the touching-sphere model. Finally, the microscopic corrections are obtained empirically and thus available only for a limited number of cluster materials. Hence, the current investigation is not meant to be a substitute for the full derivation of absolute energies and of fission dynamics from theoretical calculations. Note that fission barriers of $\mathrm{Ag}_n{}^{2+}$ have been derived by Koizumi *et al.* in a deformed liquid-drop model including (theoretical) shell corrections [24]. It would be interesting to extend these kind of calculations, which so far were performed only for very mass-symmetric fission channels, to the experimentally observed trimer fission.

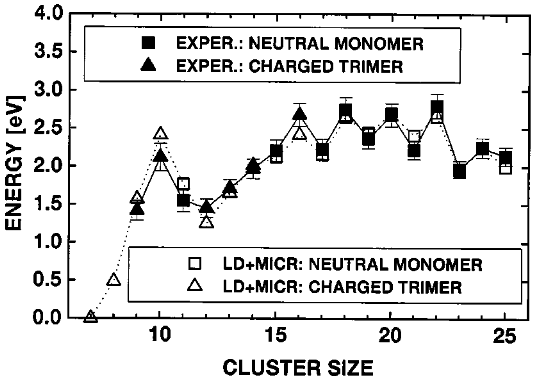

FIG. 6. Measured dissociation energies of doubly charged silver clusters (filled symbols) in comparison with the (lowest-energy) dissociation energies calculated in the liquid-drop model with empirical shell correction (open symbols).

IV. CONCLUSION AND OUTLOOK

Empirical shell corrections, deduced from measured dissociation energies of singly charged cluster cations have been successfully used to reproduce the dissociation pathways and energies of doubly charged silver cluster cations in a macroscopic-microscopic model. The present investigation emphasizes the significance of the electronic structure of silver clusters in quantitative detail and shows the power of the liquid-drop model with empirical shell corrections for the prediction of the dissociation energies of clusters of a given charge state from those of another charge state. This approach may be applied to other metals or charge states where measurements on singly charged clusters are available. In particular, one possible extension could be the application to dianionic metal clusters as recently produced at the Mainz cluster trap [42].

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