Electronic Shell Structure in Large Metallic Clusters

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The investigation of shell structure in the ground states of atoms is limited to values of the angular momentum quantum number $l \leq 3$. In atomic nuclei, shells with $l \leq 6$ can be observed. We present evidence for shell structure in the electronic states of metal clusters for $l \leq 12$.

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During the past few years it has been shown that many properties of metal clusters are amazingly similar to those of atomic nuclei. For example, giant dipole resonances have been observed in eight-atom alkali-metal clusters.[1-11] In addition, the one-particle shell model, without spin-orbit interaction, predicts very accurately trends in the ionization energies of metallic clusters containing from 8 to 92 delocalized electrons.[12-24] Nuclear physicists have long speculated about larger shells, corresponding to angular momentum quantum numbers greater than 6 in nuclei[25] and, more recently, clusters.[26] However, there is of course an upper limit to the size of atomic nuclei that can be conveniently investigated. There is no such limit on the size of metallic clusters. In this paper we present evidence for shells in the electronic structure of metal clusters, specifically Cs-O clusters and Cs-SO_2 clusters.[27]

The experiments have been carried out using a pulsed dye laser and a time-of-flight mass spectrometer. Our system now has a mass range of over 200000 amu with a mass resolution of 20000 thus allowing a detailed investigation of large shells in clusters of elements as heavy as cesium. The cluster source is a low-pressure condensation cell.[28] Cesium vapor was quenched in cold He gas having a pressure of about 1 mbar. A small amount, less than 0.02%, of either O_2 or SO_2 was added to the He-cooling gas. Apparently, Cs_2O and Cs_2SO_2 provide stable seeds onto which metal atoms can condense. Cs-O or Cs-SO_2 clusters condensed out of the quenched vapor and were transported by the gas stream through two chambers of intermediate pressure into a high-vacuum chamber where they were photoionized with a 1-μJ, 2×1-mm, 15-nsec dye laser pulse. The ion signals were linearly dependent on the dye laser power. These was no evidence for fragmentation in the high-resolution mass spectra. The time-of-flight mass spectrometer is described in detail in separate publications.[29,30]

Mass spectra of $Cs_{n+2}(SO_2)$ clusters obtained using four different dye-laser photon energies are shown in Fig. 1. Although it is not possible to distinguish the individual mass peaks in this condensed plot, it is evident that the spectra are characterized by steps. For example, a sharp increase in the mass-peak intensity occurs between $n=92$ and 93. This can be more clearly seen if the mass scale is expanded by a factor of 50 (Fig. 2). Notice also that the step occurs at the same value of n for clusters containing both one and two SO_2 molecules. In addition to the steps for $n=58$ and 92 in Fig. 1, there are broad minima in the 2.53-eV spectrum at about 140 and 200 Cs masses. These broad features become sharp steps if the ionizing photon energy is decreased to 2.43 eV. By successively decreasing the photon energy, steps can be observed for the magic numbers $n=58$, 92, 138, 198 ± 2, 263 ± 5, 341 ± 5, 443 ± 5, and 557 ± 5.[31,32] However, the steps become less well defined with increasing mass. This can be seen in Fig. 3 where the scale is again expanded by a factor of 10 in the mass range 72000–82000 amu. We have studied the mass spectra of not only $Cs_{n+2}(SO_2)$ but also $Cs_{n+4}(SO_2)_2$, $Cs_{n+2}O$, and $Cs_{n+4}O_2$. They all show steplike features for the same values of n.

First, we would like to offer a qualitative explanation

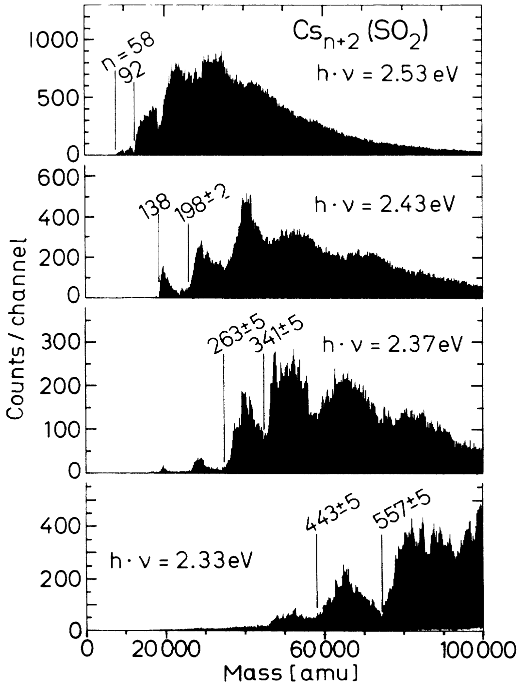

FIG. 1. Mass spectra of $Cs_{n+2}(SO_2)$ clusters with decreasing photon energy of the ionizing laser from 2.53 eV (top) to 2.33 eV (bottom). The values of n at the bottom of steps in the mass spectra have been indicated.

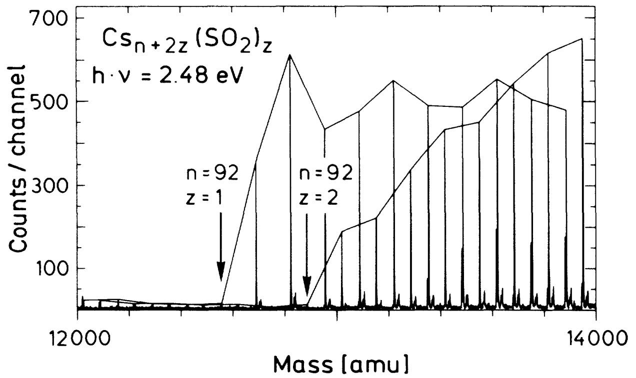

FIG. 2. Expanded mass spectra of $Cs_{n+2z}(SO_2)_z$ clusters for an ionizing photon energy of 2.48 eV. The lines connect mass peaks of clusters containing the same number z of SO_2 molecules. Notice that the steps for clusters containing SO_2 and $(SO_2)_2$ are shifted by two Cs atoms.

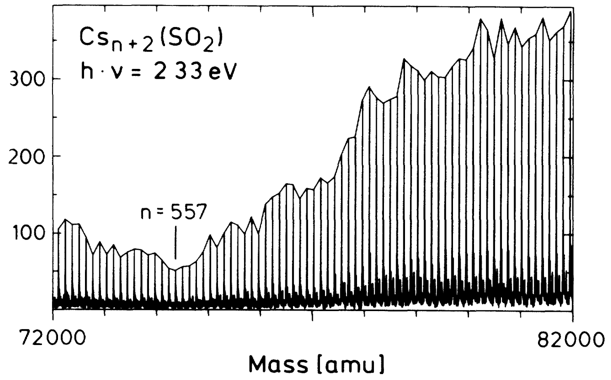

FIG. 3. Expanded mass spectrum of $Cs_{n+2}(SO_2)$ clusters for an ionizing photon energy of 2.33 eV. A mass-peak connection line is drawn for clusters containing one SO_2 molecule.

for these results and then support this explanation with detailed calculations. Each cesium atom contributes one delocalized electron which can move freely within the cluster. Each oxygen atom, and each SO_2 molecule, bonds with two of these electrons. Therefore a cluster with composition $Cs_{n+2}(SO_2)$, for example, can be said to have n delocalized electrons. The potential in which the electrons move is nearly spherically symmetric, so that the states are characterized by a well-defined angular momentum. Therefore, the delocalized electrons occupy subshells of constant angular momentum. When one of these subshells is fully populated with electrons, the ionization energy is high and the clusters will not appear in mass spectra obtained using sufficiently low ionizing photon energy.

In previous experiments the closing of small subshells of angular momentum was shown to be accompanied by a sharp step in the ionization energy for Cs-O clusters having certain sizes, namely, for $Cs_{n+2z}O_z$ with $n=8$, 18, 20, 34, 58, and 92. The closing at $n=40$ seen in all other alkali-metal clusters could not be observed, neither in the experiments nor in the calculations. The steps were observed for clusters containing from one to seven oxygen atoms. In these experiments not all predicted subshell closings could be observed. We speculated that the subshells bunch together to form shells of approximately constant energy.[24]

In the present set of experiments this bunching is confirmed and observed to continue in larger clusters. The shell structure has revealed itself as an abrupt increase in the intensity of peaks in mass spectra only for the above-mentioned numbers of electrons. This occurs when the incident photon energy is less than the ionization energy of closed-shell clusters but more than that for large, open shells.

Because of the large size of the clusters investigated, an *ab initio* calculation of the electronic properties is out of the question. In fact, we have used the simplest of models to calculate shell structure. Spin correlation and nonspherical distortions of the cluster geometry were ignored. The simplest model considered consisted of noninteracting electrons in a sphere with hard walls. The existence of the doubly charged O^{2-} central ion is recognized only by reducing the number of free electrons by two. This has been shown to be a valid approximation even in self-consistent-field calculations on Cs_nO clusters.[24] The spherical symmetry leads to highly degenerate states with energies ϵ_{ml} defined by the mth zero of the lth-order spherical Bessel function. The results are as follows: (1) One is able to identify for each experimentally observed step a possible closed-subshell configuration. This indicates that, at least in the neighborhood of magic numbers, the ordering of states must be correct. (2) In analogy to the shell model used in nuclear physics, grouping of states would lead to an explanation of magic numbers. This simplest of models shows a correct grouping of subshells for $n=8$, 20, 34, 58, 92, 138, (254), and 338. No grouping is observed for $n=198$, 440, and 562.

In a next step, we performed self-consistent calculations applying the density-functional approach to the spherical jellium model.[20,21,33] We used an exchange-correlation term of the Gunnarsson-Lundqvist form[34] and a jellium density $r_s=5.75$ corresponding to the bulk value of cesium. This model implies two improvements over the hard-sphere model. First, electron-electron interaction is included. Second, the jellium is regarded to be a more realistic simplification of the positive-ion background than the hard sphere. Again, the O^{2-} ion is taken into account only by omitting the cesium electrons presumably bound to oxygen. The calculations were performed on Cs_{600} clusters.

We found that if a homogeneous jellium was used, the grouping of subshells was rather similar to the results of the hard-sphere model. However, a nonuniform jellium yielded a shell structure in better accordance with exper-

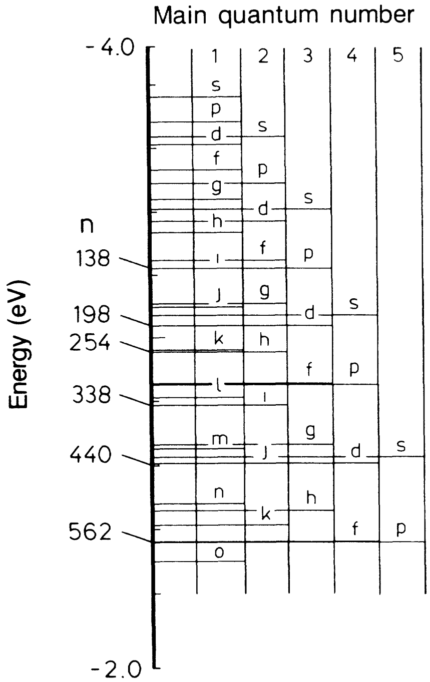

FIG. 4. The self-consistent, one-electron states of a 600-electron cluster calculated using a modified spherical-jellium background.

imental results. We found that the subshells group fairly well into the observed shells only if the background charge distribution is slightly concentrated in the central region. This was achieved, for example, by adding a weak Gaussian (0.5% total charge density, half-width of 6 a.u.) charge distribution to the uniform distribution (width 48 a.u.). Figure 4 shows the ordering of subshells obtained from the potential. This leads to the rather surprising result that the Cs^+ cores seem to have higher density in the neighborhood of the center, perhaps due to the existence of the O^{2-} ion. All attempts to lower the positive charge density in the central region led to an incorrect ordering of states.

These first two calculations address the problem of the grouping of low-lying energy levels in one large Cs_{600} cluster. However, in the experiment the magic numbers were found by a rough examination of ionization potentials of the whole distribution of cluster sizes. A more direct way to explain magic numbers is to look for steps in the ionization-potential curve of Cs-O clusters. Therefore, a third calculation has been carried out. We calculated the ionization potentials of $Cs_{n+2}O$ for $n \leq 600$ using the same local-density scheme described above (Fig. 5). Starting from a known closed-shell configuration for $n=18$, electrons were successively added. Three test configurations were calculated for each cluster size testing the opening of new subshells. The configuration with minimum total energy was chosen for the calculation of the ionization potential.

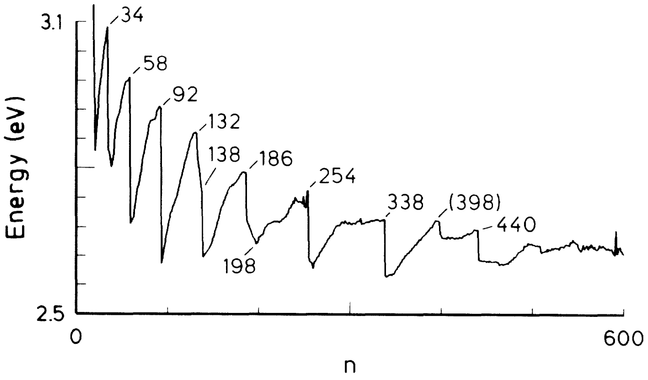

FIG. 5. Ionization potentials calculated as a function of n for $Cs_{n+2}O$ clusters. A positive background charge distribution slightly concentrated in the central region has been used.

We found that the lower magic numbers, $n=34$, 58, and 92, were well reproduced. For higher n, distinct steps in the ionization potential were observed for $n=138$, 254, 338, and 440. Smeared steps are observed for $n=132$–138 and 186–198. Only $n=562$ was not found. We want to stress that the observation of higher magic numbers would lead to a more certain prediction of the background ion potential. The fact that we could not calculate $n=562$ indicates that our basic background charge distribution has to be refined. In addition, we remark that the absolute values of the calculated ionization potentials can be brought into better agreement with experiment by assuming that clusters have a 10%–15% lower electron density than is found in the bulk.

The difference in the ionization energy of a closed-shell cluster and the next just-opened-shell cluster decreases with increasing n as seen in Fig. 5. As this difference approaches the broadening of the photoionization curve due to Frank-Condon factors, cluster temperature, isomerization, etc.,[35] the steps in the mass spectra can be expected to be smeared (Fig. 3). The mass spectra also demonstrate a great deal of reproducible structure other than the steps we have been discussing. In some cases these structures change completely in going from $Cs_{n+2}O$ to $Cs_{n+4}O_2$ or from $Cs_{n+2}O$ to $Cs_{n+2}(SO_2)$. This indicates that these structures cannot be simply explained in terms of the number of delocalized electrons. On the other hand, other structures are dependent only on n. This fine structure will be discussed in a more detailed publication.

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[27] At least two other groups are, to our knowledge, investigating large metal clusters: J. Pedersen *et al.*, at the Niels Bohr Institute in Copenhagen, and R. Whetten *et al.*, at the University of California, Los Angeles.

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[32] Since this manuscript was submitted, we have observed five additional shells in pure Na clusters, $n=700\pm15$, 840 ± 15, 1040 ± 20, 1220 ± 20, and 1430 ± 20. In addition, a new set of shells was observed extending out to $n=21\,000$. T. P. Martin, T. Bergmann, H. Göhlich, and T. Lange (to be published).

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