VOLUME 60, NUMBER 17 PHYSICAL REVIEW LETTERS 25 APRIL 1988

# Evidence of Electronic Shell Structure in Cs-O Clusters

T. Bergmann, H. Limberger, and T. P. Martin
*Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart 80, Federal Republic of Germany*
(Received 21 December 1987)

Unusually high ionization energies have been observed for Cs-O clusters having certain sizes and compositions, namely for $Cs_{2n+z}O_n$ with $z=8$, 18, 34, 58, and 92. The anomalies are well defined for clusters containing from one to seven oxygen atoms. The indicated values of $z$ are identical to the numbers of electrons in closed shells of angular momentum.

PACS numbers: 82.30.Nr, 36.40.+d

Physicists like to model reality with a sphere. This tendency has led not only to numerous jokes, but, more importantly, to notable successes in the description of physical phenomena in a simple but realistic way. Recently, it has been shown that the electronic properties of alkali-metal clusters can be described by use of a spherical potential not merely for individual atoms, but for the cluster as a whole.[1-10]

In 1981 a short paper appeared[1] predicting irregularities in the ionization potential of metal clusters as a function of size. According to the model used, metal clusters containing 8, 18, 20, 34, 40, and 58 delocalized electrons should have particularly high ionization energies. The model was based on the assumption that metal clusters, irrespective of size, have spherical symmetry. The magic numbers reflect the degeneracy, $2l+1$, of one-electron states with angular-momentum quantum number $l$.

At that time there was no experimental evidence to support this seemingly improbable description. However, three years later the evidence was provided.[3] Mass spectra of Na clusters were shown to demonstrate high peak intensities for clusters containing 8, 20, 40, and 58 atoms. These two papers seemed to indicate that the description of the electronic properties of at least alkali-metal clusters is amazingly simple.

In this paper we will present evidence that such a model may also be applicable to compound clusters composed of cesium and oxygen atoms.

Two quite different experimental arrangements were used in this investigation to ionize and detect Cs-O clusters. In one set of experiments a continuous dye laser was used for photoionization and a quadrupole mass spectrometer served as detector. This system has the advantage of a high cluster-ion counting rate and of a large dynamical range even for low peak laser power. A disadvantage of the continuous system is that our quadrupole has an upper mass limit of 2024 u and a mass resolution, $m/\Delta m$, of less than 1000. Therefore, a second set of experiments has been carried out with a pulsed dye laser and time-of-flight mass spectrometer. This system extends the mass range to over 20000 u with a mass resolution of 30,000. However, because of the high peak power levels, the laser must be strongly attenuated to suppress multiphoton processes. The laser power for both systems was, of course, reduced to levels for which the ion signals were linearly proportional to photon flux. The details of both systems will be presented in more comprehensive publications.

The cluster source was the same in both systems. Cesium vapor created in a heated glass crucible was quenched in cold He gas having a pressure of 1 mbar. The reactant, $O_2$, was introduced as a gas mixed with the helium. Clusters and microcrystals condensed out of the quenched vapor and were transported by the gas stream through a 2-mm nozzle into a chamber of intermediate pressure. After passing through a skimmer, the clusters entered a high-vacuum chamber where they were photoionized. The details of the cluster source can be found in a previous publication.[11]

With use of both the continuous and pulsed system, photoionization spectra have been recorded for hundreds of Cs-O clusters. The spectra taken with the continuous laser have a very high signal-to-noise ratio. Six different dyes were used in order to scan the wavelength over the entire range 15500–25000 $cm^{-1}$. The ion signal has been normalized to dye-laser intensity. Background signal caused by ionization from photoelectrons or from broadband fluorescence was so low that ion signals could be recorded over 5 orders of magnitude.

Photoionization spectra that consist of one sharp step can be straightforwardly interpreted. In practice the spectra are usually much more complicated. The interpretation of these spectra requires assumptions concerning the temperature of the cluster, the electronic-vibrational coupling (Franck-Condon factors), the form of the vibration-free photoionization efficiency curve, and the extent and the temperature dependence of isomerization and fragmentation. We are now in the process of analyzing hundreds of cluster photoionization spectra with respect to these points. It would be inappropriate to tabulate ionization energies at this time because the exact values would require revision as we refine our analysis.

We would like to mention the general criteria we are using to analyze the spectra. In the past cluster photoionization spectra have been presented on a linear scale allowing spectral features to be analyzed for counting rates covering 2 orders of magnitude. We have chosen to plot our counting rates over 5 orders of magnitude, thus revealing weak prethreshold signals due to fragmentation and perhaps isomerization. However, only the top 2 orders of magnitude will be discussed in this Letter. This is most conveniently done by our plotting the derivative of the experimental spectrum on, not a logarithmic scale, but a linear scale. Such a presentation automatically suppresses the much weaker prethreshold features. If we assume that the broadening in the threshold region is due to atomic motion, then the first peak in the derivative curve defines the vertical ionization energy.

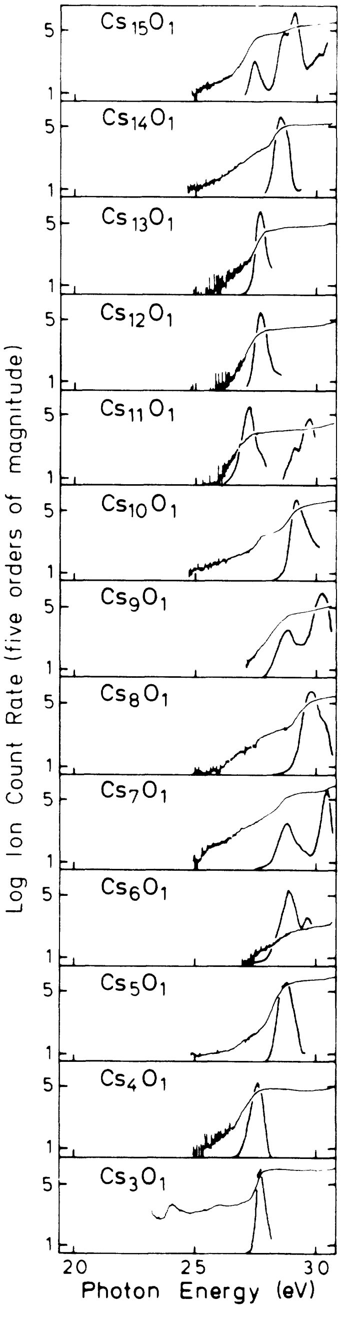

FIG. 1. Photoionization spectra (logarithmic scale) and their derivatives (linear scale) for $Cs_nO$ clusters. Notice that $Cs_{11}O$ has a particularly low energy threshold for photoionization.

The time-of-flight mass spectra indicate that there is less than 1% fragmentation taking place on the time scale accessible ($\tau > 10^{-7}$ sec). However, the limited dynamical range of the time-of-flight measurements does not allow us to investigate the prethreshold region where quadrupole measurements indicate fragmentation may well be occurring. The photoionization spectra and a complete analysis will be presented in a forthcoming detailed report.

A short series of photoionization spectra for cesium clusters containing one oxygen atom is shown in Fig. 1. If, when recording a mass spectrum, one uses laser light of 2.7 eV, then the $Cs_{11}O$ and $Cs_{15}O$ will appear anomalously strong. This is because they have the lowest threshold energies in the series. In the remaining portion of the paper, mass spectra taken with different photon energies of the laser light will be interpreted in just this way.

A time-of-flight mass spectrum of oxygen-deficient clusters from 0–15000 u contains more than one thousand mass peaks. Although each of these mass peaks is well resolved in the experiments, the limited resolution of a printed page prevents us from presenting complete mass spectra. A partial spectrum, from 4000 to 6000, is shown in Fig. 2. The lines fall in bunches. Each bunch contains a fixed number of Cs atoms with varying numbers of oxygen atoms. We have connected with a solid line those peaks corresponding to clusters containing a fixed number (two) of oxygen atoms. Notice the steep

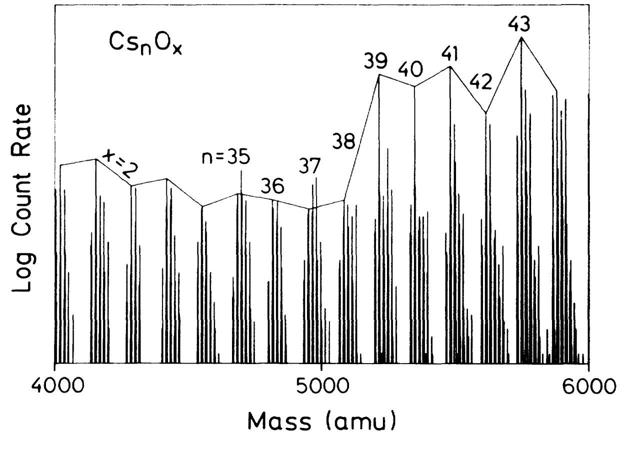

FIG. 2. Portion of a high-resolution time-of-flight mass spectrum of Cs-O clusters photoionized with 480-nm laser light. The mass peaks of clusters containing two oxygen atoms have been connected.

increase in intensity between $Cs_{38}O_2$ and $Cs_{39}O_2$. In order to recognize such features more easily, a series of such connection lines are shown in Figs. 3 and 4.

Figure 3 shows the mass peak connection lines for $Cs_nO_x$ clusters obtained with a laser wavelength of 480 nm. Notice the sharp increase in intensity for $x=2$ in going from $Cs_{22}O_2$ to $Cs_{23}O_2$ and from $Cs_{38}O_2$ to $Cs_{39}O_2$. These steps also appear in the connection lines for $x=3$. However, the steps are shifted by two cesium masses. The steps also occur for $x=4$ and 5, however, successively shifted by two cesium masses. In addition to these steplike features, there are broad minima for clusters containing between sixty and seventy cesium atoms. Tuning of the dye laser wavelength from 480 to 500 nm results in a transformation of the broad minima into sharp steps and also in the appearance of a new set of minima for clusters containing from 90 to 100 cesium atoms (Fig. 4). To summarize these data, sharp steps are observed in the mass-peak connection lines of $Cs_{2n+z}O_n$ clusters for $z=8$, 18, 34, and 58. Broader features are observed for values of $z$ between 90 and 92.

The interpretation of mass spectra alone is not necessarily straightforward because several factors influence mass-peak intensities; photoionization cross section, neutral-cluster distribution, and the stability of ionized fragments. The interplay among these factors is easily observed as the experimental conditions are varied. For example, if a very high laser fluence is used, multiphoton processes lead to extensive fragmentation. Under such conditions mass spectra will reflect the relative stability of the fragments. In the present case, this means that mass peaks corresponding to open-shell configurations will be *weak*. However, if low laser fluence and long wavelengths are used, open-shell configurations have large cross sections for ionization and their mass peaks will be particularly *strong*. Both effects have been observed in our investigations. However, we will limit the following discussion to the interpretation of spectra obtained with low laser fluence.

Qualitatively one can think that each oxygen atom bonds two electrons from a sea of delocalized electrons in a Cs cluster. With use of this picture $Cs_{38}O_2$, $Cs_{40}O_3$, $Cs_{42}O_4$, etc., would be said to contain 34 delocalized electrons. Our photoionization spectra show that such clusters have high ionization energies. The clusters $Cs_{39}O_2$, $Cs_{41}O_3$, $Cs_{43}O_4$, etc., contain 35 electrons and

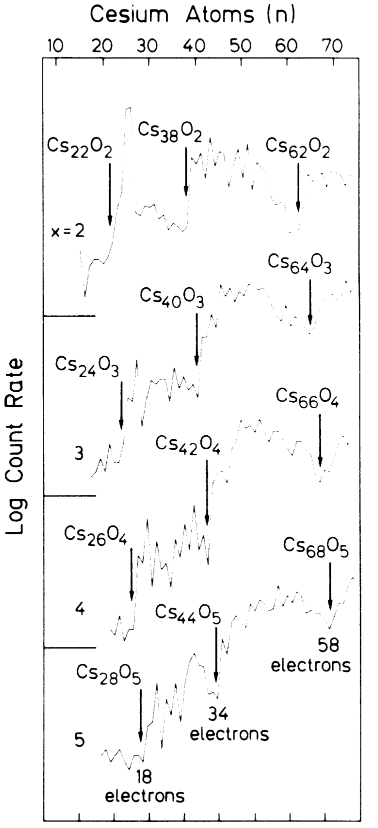

FIG. 3. Mass peak connection lines for $Cs_nO_x$ clusters photoionized with 480-nm laser light. Notice that the positions of the characteristic steps depend on the number of oxygen atoms.

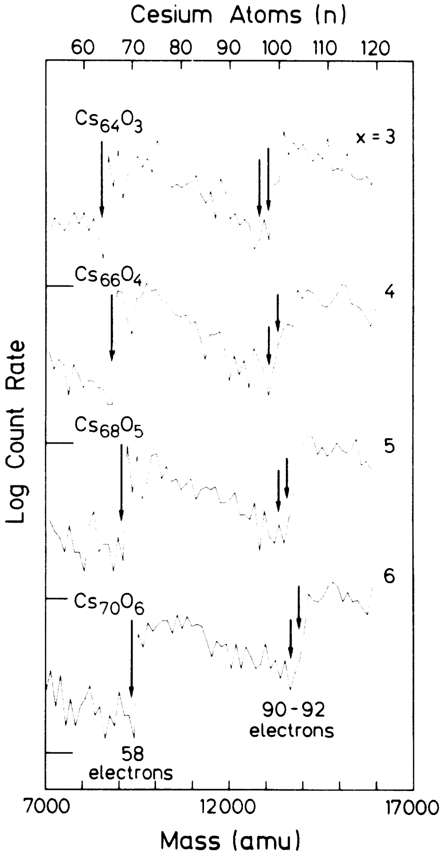

FIG. 4. Mass peak connection lines for $Cs_nO_x$ clusters photoionized with 500-nm laser light.

are observed to have relatively low ionization energies. By choosing the laser photon energy to lie between the sets of high and low ionization energies, we have been able to demonstrate, by means of mass spectra, that clusters containing 8, 18, 34, 58, and 92 delocalized electrons are much more difficult to ionize than the corresponding clusters containing one more electron.

The form of the radial dependence of the potential energy determines the ionization energy for each shell. For example, the potential used in Ref. 1 predicts almost no change in the ionization energy on opening of the 2*s* and 2*p* shells. Perhaps coincidentally, we also observe no strong anomalies for clusters containing 21 and 41 delocalized electrons. In fact, an appreciable lowering of the ionization energy is observed for only the 41-electron cluster containing one oxygen atom. In general, all anomalies become less distinct with increasing oxygen content.

These results are consistent with the following simple interpretation. Clusters with composition $Cs_{z+2n}O_n$ have $z$ delocalized electrons which can apparently be described as moving a spherical potential, just as in pure alkali-metal clusters. The orbitals are defined by angular momentum $l$ and the observed anomalies in the mass spectra correspond to electron configurations $(1s,1p)$; $(1s,1p,1d)$; $(1s,1p,1d,2s,1f)$; $(1s,1p,1d,2s,1f,2p,1g)$; $(1s,1p,1d,2s,1f,2p,1g,2d,1h,3s)$.

If the delocalized electrons move in a spherical potential in Cs-O clusters, it is interesting to speculate about the form of this potential. One possibility is that $Cs_{2n}O_n$ forms a "nonconducting" spherical core within the cluster. The remaining cesium atoms arrange themselves into a shell around this core. In this picture the excess electrons can be described as moving in a spherical shell potential.

---

[1] J. L. Martins, R. Car, and J. Buttet, Surf. Sci. **106**, 265 (1981).

[2] W. Ekardt, Ber. Bunsenges. Phys. Chem. **88**, 289 (1984).

[3] W. D. Knight, K. Clemenger, W. A. Heer, W. A. Saunders, M. Y. Chou, and M. L. Cohen, Phys. Rev. Lett. **52**, 2141 (1984).

[4] W. Begemann, S. Dreihofer, K. H. Meiwes-Broer, and H. O. Lutz, Z. Phys. D **3**, 183 (1986).

[5] I. Katakuse, I. Ichihara, Y. Fujita, T. Matsuo, T. Sakurai, and T. Matsuda, Int. J. Mass Spectrom. Ion Processes **67**, 229 (1985).

[6] A. Herrmann, E. Schumacher and L. Wöste, J. Chem. Phy. **68**, 2327 (1978).

[7] M. M. Kappes, R. W. Kunz, and E. Schumacher, Chem. Phys. Lett **91**, 413 (1982).

[8] K. I. Peterson, P. D. Dao, R. W. Farley, and A. W. Castleman, Jr., J. Chem. Phys. **80**, 1780 (1984).

[9] C. Bréchignac, Ph. Cahuzac, and J.-Ph. Roux, Chem. Phys. Lett. **127**, 445 (1986).

[10] W. A. Saunders, K. Clemenger, W. A. de Heer, and W. D. Knight, Phys. Rev. B **32**, 1366 (1985).

[11] T. P. Martin, J. Chem. Phys. **81**, 4426 (1984).