

Variable surface composition and radial interface formation in self-assembled free, mixed Ar/Xe clusters

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Using photoelectron spectroscopy, we demonstrate how the self-assembling process of cluster formation in an adiabatic expansion leads to radial segregation and layering as well as to variable surface composition for binary Ar/Xe clusters. The radial structuring can be qualitatively understood from the different interatomic bonding strengths of the two components.

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¹Clusters are polyatomic aggregates between isolated atoms and bulk solids [1]. Physical and chemical properties of clusters often change radically with size, and the possibility to tune these properties by changing the size is one of the main reasons for the interest in clusters. In addition, when a cluster contains more than one element, the spatial distribution of different components creates one more degree of freedom defining the properties. Finding methods capable to determine the structure of clusters as a function of size and composition is a task of large potential importance.

Van der Waals (vdW)-bonded clusters have served as important model systems for cluster science. In these systems several phenomena of general significance, such as magic numbers [2], were discovered first. One reason for the interest in vdW clusters is the nondirectionality of the vdW bond, a property it shares with the metallic bond. Both vdW and metal clusters form close packed, radially layered structures, which minimize the total free energy by minimizing the fraction of surface atoms.

Mixed clusters offer more possibilities for tunable properties than homogeneous clusters, since not only the size but also the stoichiometry and the spatial distribution of the components can vary. Mixed clusters can be seen as nanoversions of solid solutions, alloys and compound solids. For such systems, surface segregation is a known phenomenon [3]. The simplest explanation for this is that the total energy of the system is minimized by surface enrichment of the element with the lowest cohesive energy. The importance of the surface for clusters accentuates these issues for the structure of mixed clusters, as illustrated by theoretical studies of bimetallic clusters [4]. The structural similarity between vdW and metallic clusters motivates the study of mixed vdW clusters as a way of gaining insight into bimetallic clusters.

VdW clusters can be formed by adiabatic expansion of high-pressure gas through a narrow nozzle into vacuum. A one-component expansion produces a distribution of cluster

sizes around a certain average size, determined by several factors: the bonding strength between the monomers, the gas pressure and the nozzle temperature and geometry [5,6]. Mixed clusters can be formed by either coexpansion of a gas mixture, as done in this work, or by doping of single-component clusters in a secondary pick-up process, as exemplified by Refs. [7,8]. The cluster formation process in the coexpansion of a binary mixture is less well known than in the one-component case. In addition to the factors important for the one-component expansion, it can be expected that the *A-A*, *A-B*, and *B-B* bonding strengths, as well as the primary *A/B* ratio in the gas mixture, will influence the cluster size and composition. These expectations are supported by molecular dynamics simulations of mixed rare-gas clusters, which suggest a complex dependence of the cluster structure upon the relative interatomic distances and bonding strengths [9,10]. The resulting cluster structures may also depend on the mode of production. For instance, simulations of the doping of single-component clusters in a secondary pick-up process suggest that the resulting binary clusters do not reach the lowest-energy structure [11].

In this paper we present an experimental study using high-resolution x-ray photoelectron spectroscopy (XPS) of mixed Ar/Xe clusters produced by coexpansion of argon and xenon gas in different mixing ratios. XPS is a local probe, able to distinguish atoms of the same element with different local surroundings, utilizing the atomlike nature of core orbitals [12]. For free clusters it is possible to separate spectral components from “bulk” and surface atoms [13–15]. XPS thus has the capability to probe the spatial distribution of the two components in the mixed Ar/Xe clusters. After careful analysis of the spectra as a function of primary Ar/Xe mixing ratio, we here present a model for the structure of these binary clusters. The model includes radial segregation leading to layering and interface formation, as well as to variable surface composition for the Ar/Xe clusters. The suggested structure is qualitatively discussed using the different interatomic bonding strengths of the two components.

Clusters were produced by adiabatic expansion of 2.5 bar gas mixtures of Ar/Xe through a narrow conical nozzle (throat diameter 150 μm , total opening angle 10°, tempera-

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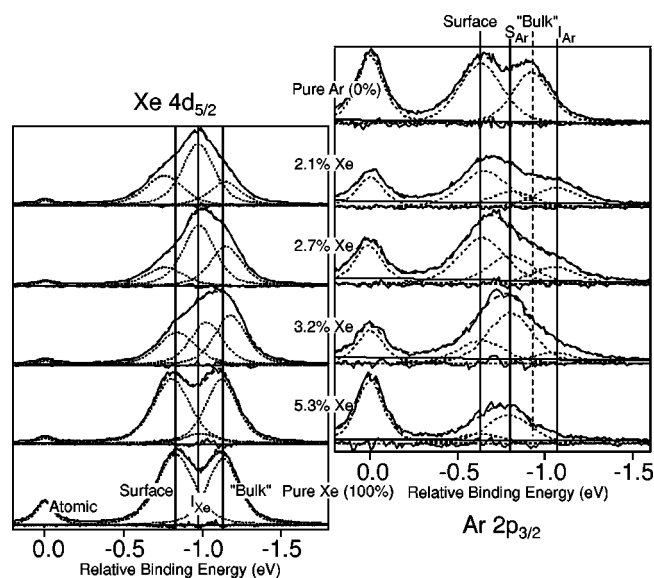


FIG. 1. XPS spectra of the Ar $2p_{3/2}$ and Xe $4d_{5/2}$ core levels for clusters produced from different primary gas mixing ratios. The peak at $\Delta E_B = 0$ corresponds to the atomic peak with the same total momentum as the cluster features.

ture -20°C) into vacuum [16]. Ar/Xe mixtures of varying ratios were prepared by mixing controlled amounts of the separate high-purity gases from high-pressure cylinders in low-pressure bottles. XPS spectra were recorded at the undulator beamline I411 of the Swedish synchrotron facility MAX-lab [17], using a modified Zeiss SX-700 monochromator and a Scienta SES-200 photoelectron spectrometer. The spectra were recorded in the plane normal to the photon beam, at 90° relative to the polarization direction of the radiation. The total experimental resolution was ≈ 120 meV for Ar $2p$ and ≈ 50 meV for Xe $4d$. The short mean free path of electrons in condensed matter makes XPS highly surface sensitive [12]. The photon energies were chosen so that both Ar and Xe photoelectrons from the clusters had 50 eV kinetic energy, ensuring similar surface sensitivity. The spectra have been fitted using Voigt peaks with Lorentzian widths corresponding to the atomic lifetime width and Gaussian widths similar to those found for the pure clusters. We would like to stress that the measurements were performed on a beam of mixed clusters, which contains clusters within a range of size and composition. We cannot study individual clusters, and our results should therefore be seen as describing the “average” cluster produced under different conditions.

In Fig. 1 XPS spectra of the Ar $2p$ and Xe $4d$ core levels are presented for several ratios of the primary Ar/Xe gas mixture with the other factors influencing the cluster formation kept constant. Even though the primary mixture may contain very little xenon, the percentage of Xe clusters in the produced cluster may be higher. The reason is higher bonding probability for Xe. The mixing ratios in Fig. 1 thus refer to the primary composition.

The peaks at relative binding energy (ΔE_B) of 0 eV are due to uncondensed atoms, and the structures at lower binding energies are due to clusters. The spectra resulting from

expansion of pure Ar (0%) and pure Xe (100%) gas exhibit two peaks due to clusters. Cluster formation is manifested as a lowering of the core level binding energy relative to the isolated atom due to polarization screening of the ionic final state [13,14]. The polarization screening depends on the coordination and distance to neighboring atoms, but is dominated by the effects from the nearest neighbors. Surface atoms have lower coordination than bulk atoms, in particular they have fewer nearest neighbors. The peak at smaller ΔE_B thus corresponds to the atoms at the cluster surface, whereas the peak at larger ΔE_B is due to electrons from the bulk atoms. For pure Ar and Xe clusters, the spectra for all sizes exhibit these two structures, and the main size dependence is a gradual increase of the bulk/surface intensity ratio with increasing cluster size [15]. The surface and bulk peaks are readily identified also in the spectra of clusters produced from Ar/Xe gas mixtures.

The first question to address is whether the clusters formed from a mixture consist of one or both elements. For the investigated range of Ar/Xe primary gas mixtures, the produced clusters exhibit more complex spectral profiles than the pure clusters. These spectra are not explainable by two components only, as was the case for the pure clusters, but (at least) three peaks are required. For low mixing ratios of Xe to Ar, the spectra are dominated by peaks which do not correspond to the surface peak or the bulk peak of the pure clusters. In addition to the XPS method, we have addressed this question using valence photoelectron spectroscopy, x-ray-absorption spectroscopy, and time-of-flight mass spectroscopy. The results from all these techniques point in the same direction: Under the investigated conditions, mixed Ar-Xe clusters are predominantly produced. The concentration levels of nonmixed clusters are too low to affect the main conclusions of this work.

The next question is the spatial distribution of Ar and Xe in the mixed clusters. In the “infinite” solid, Ar and Xe have been considered to be freely miscible, but recent results suggest microscopically separated fcc phases [18]. What happens in clusters, when the solid is far from infinite? The spectra exhibit complex changes with varying Ar/Xe mixing ratios of the primary gas. To understand these changes, let us first return to the spectra of pure Ar (0%) and Xe (100%) clusters in Fig. 1. The binding energy shift ΔE_B between a free atom and an atom in the cluster bulk is approximately -1.1 eV for Xe and -0.9 eV for Ar. For surface atoms we find $\Delta E_B \approx -0.8$ eV and -0.6 eV for Xe and Ar, respectively [19]. The larger shifts for Xe are due to the higher polarizability of Xe, an atomic property largely connected to the number of electrons and their binding energies. The more efficient screening by Xe than Ar is important to understand the present results. The ΔE_B of the pure clusters can be used to make some semiquantitative predictions for the mixed clusters. Ar atoms coordinated to Xe will have a larger negative binding energy shift than if coordinated only to Ar. Xe atoms coordinated to Ar will instead have a smaller negative binding energy shift than if coordinated to Xe. Bulk Ar atoms with mixed Ar-Xe coordination would thus reveal themselves by a peak at a ΔE_B intermediate to those of pure bulk Ar (-0.9 eV), and that of pure bulk Xe (-1.1 eV), i.e., around $\Delta E_B \approx -1.0$ eV. Both Ar and Xe surface atoms with

mixed Ar-Xe coordination would similarly display peaks at $\Delta E_B \approx -0.7$ eV. The spectral signature of bulk Xe atoms with mixed Ar-Xe coordination would be a peak at $\Delta E_B \approx -1.0$ eV. These simple considerations will be helpful to interpret the spectra for the Ar/Xe mixed clusters.

As the next step, examine the development of the XP spectra in the Xe $4d$ region. As the Xe/Ar ratio decreases, a new spectral peak emerges at $\Delta E_B \approx -1.0$ eV (I_{Xe} in Fig. 1, spectra from 5.3% to 2.1% Xe), i.e., intermediate to the Xe surface and bulk peaks. This ΔE_B value is close to the one predicted for Xe atoms in the bulk with a high coordination to Ar. This intermediate peak, which we denote I_{Xe} , gradually becomes dominant as the Xe fraction in the mixture decreases.

Now take the spectra in the Ar $2p$ region into account. For the mixed clusters, instead of the Ar surface and bulk peaks seen in the pure Ar spectrum, there is a different structure, which gradually changes with Xe/Ar ratio, and which is well described by three peaks. There is hardly any presence of the pure Ar bulk for all mixing ratios (Fig. 1), while the pure Ar surface feature is present in all but the last (5.3% Xe) spectra. (This pattern is a strong indication that mostly mixed clusters are formed.) At higher Xe/Ar fractions (3.2% and 5.3% Xe) a peak at $\Delta E_B \approx -0.7$ eV (S_{Ar} in Fig. 1), i.e., close to the predicted position for the surface Ar atoms with mixed Ar-Xe coordination, is dominant. At 2.7% of Xe in the initial ratio a peak at $\Delta E_B \approx -1.1$ eV, close to that predicted for the bulk Ar atoms with mixed Ar-Xe coordination is observed. And indeed its relative intensity grows with the increase of Ar concentration (2.1% of Xe). Similarly to the Xe case, we denote this I_{Ar} .

For further understanding, consider the Ar and Xe spectra together. For the highest presented Xe/Ar ratio (5.3%), the Ar spectrum is strongly dominated by the S_{Ar} peak due to surface Ar atoms with mixed Ar-Xe coordination, whereas in the corresponding Xe spectrum the surface and bulk peaks are of similar intensity. Also for the 3.2% case, the main contribution to Ar spectrum is this mixed coordination surface peak S_{Ar} . The larger amount of Ar atoms located at the surface of the clusters causes a major redistribution among the Xe peaks. The pure Xe surface peak decreases in relative intensity, while the intermediate I_{Xe} peak, connected to Xe atoms in the bulk with mixed coordination increases. The intermediate I_{Xe} peak is thus connected to the presence of Ar atoms on the surface, but at the same time it is due to Xe atoms that are *not* on the surface. Based on this, we interpret the I_{Xe} peak as due to Xe atoms in an interface layer between the Xe bulk and Ar surface layer(s). The S_{Ar} peak due to surface Ar atoms with mixed Ar-Xe coordination is then due to Ar atoms forming a surface layer outside the Xe interface layer, see case II in Fig. 2. This indicates that the Ar/Xe clusters are not homogeneously mixed, but rather highly segregated with a central Xe core and Ar atoms partially covering the surface.

What happens with further decrease of the Xe/Ar ratio in the primary gas mixture? The Xe spectra exhibit a continued trend towards further replacement of the surface peak by the I_{Xe} interface peak. This is reasonable, as successively more Ar is available to cover the Xe surface. In parallel to this development, the initially dominant S_{Ar} peak gradually be-

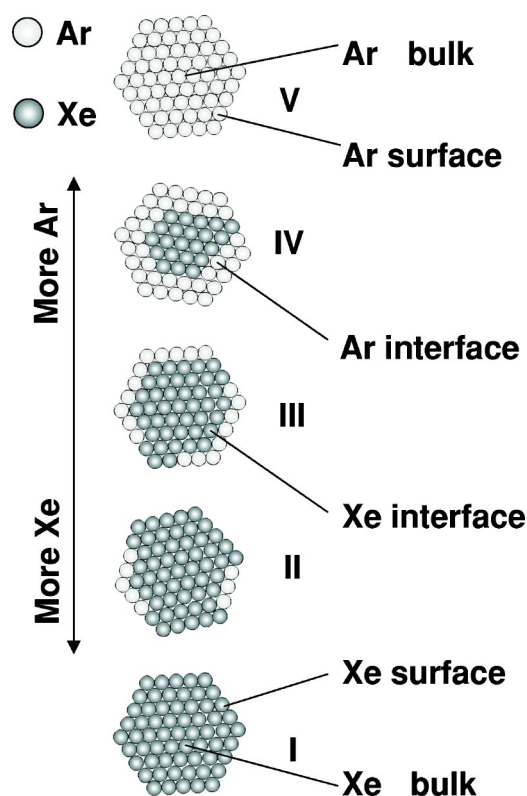


FIG. 2. A schematic illustration of the structural development of the Ar/Xe clusters, from pure Xe (I) to pure Ar (V). In cases II and III, there are, in addition to the Xe surface and bulk atoms, Ar atoms sitting on the surface coordinated with Xe and Xe atoms sitting in the bulk coordinated to the surface Ar atoms, forming an interface layer. In case IV, with more Ar, there will in addition be Ar surface atoms coordinated to Ar, as in a pure Ar cluster.

comes replaced by the Ar surface and I_{Ar} peaks. The shift of the $\Delta E_B \approx -1.1$ eV for the I_{Ar} peak is close to that predicted for bulk Ar atoms with mixed Ar-Xe coordination. This emergence of the surface peak suggests that instead of Ar adsorbing on a Xe core, as in the lower Ar/Xe ratio cases, the Ar surface atoms are now typically situated on an already existing Ar layer. We interpret this as a manifestation of the formation of successive Ar layers outside the Xe core, see case IV in Fig. 2. The nonsurface Ar atoms with substantial Xe coordination represented by the I_{Ar} peak are thus due to Ar atoms between an outermost Ar layer and the Xe core, suggesting a buried Ar/Xe interface. At the primary mixing ratio of 2.7%, the Xe surface peak is surprisingly weak, bearing in mind that XPS at 50 eV kinetic energy is highly surface sensitive [12]. The cluster surface is thus strongly dominated by Ar, which is mostly situated outside the Ar interface layer. The inferred development of the structure is schematically summarized in Fig. 2. The surface composition is thus changed from Xe on Xe (I), over Ar on Xe (II-III), to Ar on Ar (IV). For the lowest investigated Xe/Ar mixing ratios, a small energy shift of the Xe surface peak towards the atomic peak can be seen in Fig. 1. This may indicate that some surface Xe has high Ar coordination, as could be the case for Xe outside an Ar layer.

For the proposed, relatively well-ordered structure with a

Xe core surrounded by Ar atoms, two criteria must be fulfilled. The structure must be a low-energy configuration, and it must be possible to reach this configuration. The first criterion can be discussed in terms of total energy. Condensation of a group of atoms lowers its total energy. This energy lowering is known as the cohesive energy, and the cohesive energy per atom is larger for an atom in the bulk than for an atom on the surface due to the higher number of nearest neighbors in the bulk. The lower cohesive energy for surface atoms relative to bulk atoms can be regarded as an energy cost known as the surface energy. To minimize the total energy, clusters thus often adopt quasispherical shapes, minimizing the fraction of atoms at the surface. As a first approximation, the surface energy is proportional to the fraction of “missing” bonds for the surface atoms and the cohesive energy. In analogy to surface segregation in solids, it is thus energetically advantageous for mixed clusters, such as Ar/Xe, to have the atoms with the lower cohesive energy, in this case Ar, on the surface, and the high cohesive energy atoms, in this case Xe, in the bulk. To also fulfill the second criterion, the possibility to reach the low(est)-energy structure, there has to be sufficient initial mobility of the atoms in the cluster followed by cooling. Clusters formed in an adiabatic expansion are initially “boiling hot” [20], implying efficient diffusion. Evaporation of atoms gradually leads to cooling, which efficiently anneals the cluster. We find that both criteria are fulfilled: the structure proposed from analy-

sis of the XPS spectra is a low-energy structure possible to be reached in the cluster formation process.

In conclusion, we have demonstrated how the self-assembling process of mixed cluster formation can lead to radial segregation and layering as well as to variable surface composition. These phenomena can be varied using the expansion conditions and effectively monitored by synchrotron-radiation-excited core-level photoelectron spectroscopy. The radial layering can be qualitatively understood considering the difference in cohesive energies of the two constituents; in order to minimize the surface energy the high-cohesive energy component forms a core surrounded by the low-cohesive energy component. The mixed rare-gas clusters studied here may be regarded as an important step towards other radially layered clusters, in which more complex phenomena related to the electronic structure could be envisaged.

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