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Auger Electron Spectroscopy of Free Argon Clusters

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Abstract. Auger electron spectra and Auger yields of free argon clusters in the Ar(2p) excitation regime are reported. The Auger yield spectra show characteristic changes as a function of cluster size. The results indicate that the Auger yield signal originates primarily from the surface of the clusters. The results are compared to bulk-sensitive experimental techniques, such as total electron yields (TEY), zero kinetic energy electron (ZEKE) spectra for variable size clusters, as well as Auger yield spectra of condensed argon multilayers.

Introduction

Free clusters have been investigated in the past as microscopic model systems for investigating size-dependent properties (1, 2). Rare gas clusters are ideal test cases for the investigation of surface and bulk properties of variable size species. Resonant excitation of surface and bulk excitons in the VUV - and x-ray-regimes can be used to distinguish between surface and bulk properties (3, 5). Structural information from free clusters can also be obtained in the soft x-ray regime from extended x-ray absorption fine structure (EXAFS) spectroscopy (5, 6). Nearest neighbor distances and coordination numbers have been determined through the application of the EXAFS analysis. Information about structural and dynamical disorder in free clusters, due to the increased Debye-Waller factor in comparison with the condensed phase, can also be obtained (5). The structure of clusters are of considerable importance because this affects electronic structure and configurational energies. Apart from calculations and a very few number of electron diffraction experiments (7), there is little known about the structures of clusters. Virtually nothing is known from experiments about the size dependent variations in cluster structure, besides first results from EXAFS spectroscopy (5, 6).

Most elements are not as likely as the noble gases to show differences between the surface and the bulk. This is because the other elements are dominated by band structure effects which smear the local signature of the electronic structure, unlike rare gases which form Einsteinian condensates. Within the perspective of bands, increasing the screening charge surrounding a core hole shortens the lifetime of a core-exciton or permits a core exciton to unbind (8). The consequence of this

picture is that with increased electron delocalization, resonant photoemission intensities decrease intra-atomic excitations leading to the formation of a core-exciton followed by Auger decay. Such behavior has been observed with core levels across the nonmetal to metal transition for thin films and 2-dimensional overlayers (8, 9) as well as Hg clusters (10). With rare gas-metal mixtures this effect is particularly pronounced. Wannier excitons of xenon in Hg/Xe mixtures are broadened and decrease in intensity with the onset of metalicity and short range screening (11). Thus the characterization of the size dependence of cluster excitons of rare gas clusters is important to understand in detail the phenomena in the solid state.

In this paper we report the results of Auger electron spectroscopy to variable size argon clusters in the regime of the Ar(2p)-edge (240-260 eV). The goal of this work is to investigate characteristic changes of Auger electron yields as a probe of electronic relaxation in the regime of core-excitons as a function of cluster size in comparison with zero kinetic electron energy (ZEKE) spectroscopy, total electron yields, and results from absorption spectroscopy of condensed argon.

Experimental

The experimental setup consisted of a continuous supersonic jet expansion, synchrotron radiation as a tuneable soft x-ray source, a cylindrical mirror electron analyzer (CMA), and a time-of-flight mass spectrometer. Most of the details of this setup have been described earlier (4, 5).

The electron energy analyzer was a 3 cm diameter (inner diameter of the outer cylinder) single pass cylindrical mirror analyzer schematically shown in Figure 1. The analyzer design was based upon the scheme outlined by Aksela and others (12). Due to the very compact size of this analyzer, it was mounted on a linear

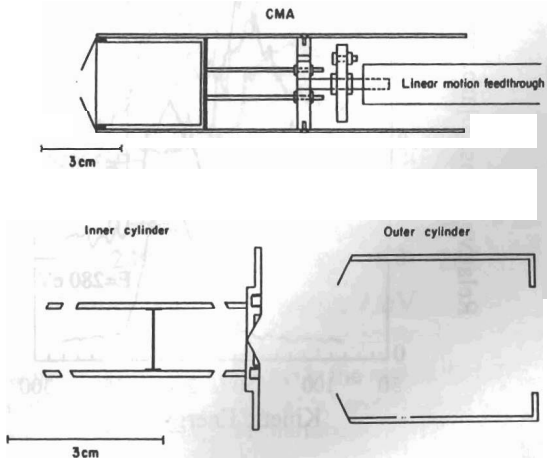

Figure 1. Schematic outlines of the inner and outer cylinders of the CMA. The drawing of the composite assembled of the CMA is also shown.

feedthrough for ease of optimizing the sample-plane to analyzer distance. Under conditions close to ideal (small sample spot size i.e. nearly point-like source for generated electrons and nearly flat sample plane of narrow sample width of a few Ångstroms), the analyzer was found to have the instrumental line width ($\Delta E/E$) of 1.5% based upon electron scattering from the surface of a single crystal of Ni(100). Using less focused incident excitation sources and sample volumes of finite width (on the order of 1 mm), the effective experimental resolution was found to be substantially worse.

Free clusters of an average cluster size between 1 and 700 atoms were excited with monochromatized synchrotron radiation from the HE-TGM-2 beam line at the storage ring BESSY (Berlin, Germany). Average cluster sizes $\overline{N}$ were estimated by correlating the reduced scaling parameter Γ^* (13) with experimental average cluster sizes (14, 15). Further details which characterize the cluster size distribution in our experiment can be found in ref. (4). A time-of-flight mass spectrometer as well as a total electron yield detector was used for aligning the jet expansion with respect to the soft x-ray beam. The total electron yield detector was then replaced by a small cylindrical mirror analyzer (CMA) for measurements of Auger electron spectra and Auger yields as a function of excitation energy. The advantage of this device is its compact size and high transmission despite limited energy resolution.

Results and Discussion

Figure 2 shows typical Auger spectra from the CMA for expansion conditions where no clusters are present in the jet. The broad feature centered at approximately 210 eV kinetic electron energy is found independent of the photon energy and is

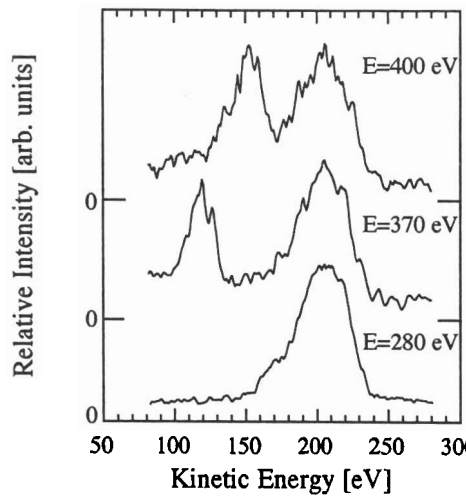

Figure 2. Auger electron spectra of atomic argon acquired at different excitation energies.

therefore assigned to the well-known LMM-Auger process (16). The broad structure indicates that the energy resolution of the CMA is too low to resolve individual Auger lines. Another signal occurs at lower kinetic energy which is dependent on the excitation energy. This is assigned to the Ar(2p) photoelectron signal, which occurs for excitations at 370 eV and 400 eV and is within the range of kinetic energies shown in Figure 2. The spectral shape is found to be unchanged, within the given resolution of the CMA, as the average cluster size is increased. This is in agreement with the results of photoelectron and Auger spectroscopy of condensed and clustered argon, where small shifts relative to the atomic value are found for the Ar(2p) ionization energies (17). For solid argon the Auger lines broaden, but do not shift (18).

Figure 3 shows Auger electron yield spectra recorded at different cluster sizes $\overline{N}$. The atomic spectrum ($\overline{N}$=1) is similar in shape to the total electron yield (4). Discrete resonances are found in the near-edge regime at 244.4 eV and 246.9 eV, corresponding to resonant excitations into Rydberg states ($Ar(2p)_{3/2}\rightarrow 4s$ and $Ar(2p)_{3/2}\rightarrow 3d$, respectively), as well as high intensity in the Ar(2p) continuum.

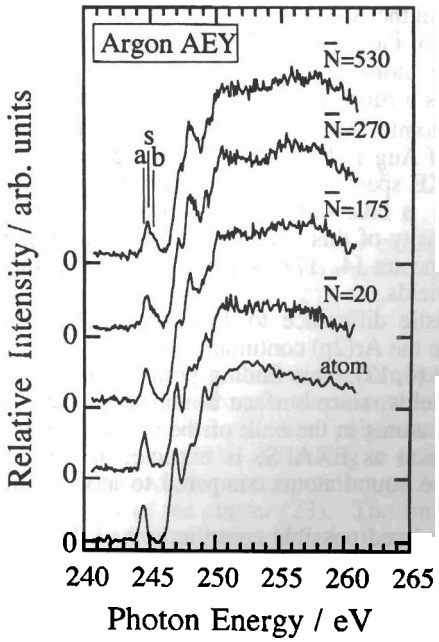

Figure 3. Auger electron yields (AEY) recorded in the regime of the Ar (2p) excitation at different average cluster sizes $\overline{N}$. The labels 'a,' 's,' and 'b' denote the energy positions of the atomic, surface, and bulk $Ar(2p)_{3/2}\rightarrow 4s$ transitions.

Spectral changes are observed as the average cluster size is increased. These concern (i) the energy position of the $Ar(2p)_{3/2}\rightarrow 4s$ transition, (ii) the appearance of

a broad exciton line at 248 eV ($Ar(2p)_{3/2}\rightarrow 3d$) connected with the disappearance of the atomic $Ar(2p)_{3/2}\rightarrow 3d$)–Rydberg transition, and (iii) weak oscillations in the Ar(2p) continuum. These changes are discussed in the following:

Total electron and partial cation yield spectra of variable size argon clusters have indicated that surface and bulk excitons can be identified by their energy positions (4, 19). This is especially true for the lowest $Ar(2p)_{3/2}\rightarrow 4s$ transition, since it is an isolated Frenkel-type exciton (20). Small blue-shifts of ≈0.35 eV are observed for surface excitons, whereas bulk core excitons are blue-shifted by ≈1 eV, as observed for the solid (20). For large clusters ($\overline{N}$=530) the maximum of the lowest exciton state at 244.8 eV shows a shift which is typical for surface excitons, contrary to total electron yield and ZEKE yields recorded under identical expansion conditions where the contribution of bulk excitons dominates (4, 17). We point out that total electron yield spectra, as well as ZEKE yield spectra, do not reflect the actual surface-to-bulk ratio of the neutral cluster size distribution since both techniques are particularly sensitive to those electrons which have low kinetic energy. We have shown earlier that low kinetic energy photoelectrons stem from inelastic scattering processes within the clusters (17), i.e. from the bulk. This is evidently not the case for Auger electrons. The maximum of the $Ar(2p)_{3/2}\rightarrow 4s$ transition at 244.8 eV in the Auger yield spectra shows therefore clear evidence for the surface sensitivity of the Auger yields (cf. Figure 3).

A blue-shift of the atomic $Ar(2p)_{3/2}\rightarrow 3d$–Rydberg transition occurring at ≈247 eV is also observed as a function of cluster size. However, this blue-shift is less clear than for the atomic $Ar(2p)_{3/2}\rightarrow 4s$–transition because of the underlying continuous intensity of Auger electrons in this energy regime. We observe, as in the case of TEY and ZEKE spectra for large cluster sizes a distinct resonance at 248 eV, corresponding to a blue-shift of 1 eV, which is typical for bulk excitons. Interestingly, the intensity of this feature is weaker for Auger yields, as compared to TEY and ZEKE spectra (4, 17), which is another indication for the surface sensitivity of Auger yields.

Another characteristic difference to TEY and ZEKE spectra concerns weak EXAFS oscillations in the Ar(2p) continuum, where the first pronounced maximum is observed at 256 eV (4, 17). This finding points also to the surface sensitivity of the Auger electron yields, since surface bound atoms are expected to have less neighbors than argon atoms in the bulk of the cluster. As a consequence, a single scattering process, such as EXAFS, is expected to result in weaker intensity oscillations for surface bound atoms compared to atoms which are located in the bulk of the clusters.

We have also considered possible contributions of Auger electrons which come from the outer part of the cluster beam containing mostly atoms. In order to estimate this possible contribution of the atomic component, we have subtracted a contribution of 40% of the atomic spectrum from that corresponding to $\overline{N}$=530. The resulting spectrum is compared in Figure 4 to the multilayer spectrum of condensed argon recorded by Rocker *et al.* (21). Both spectra are now more similar in shape, however differences are still evident: (i) in the regime of the lowest exciton (E≈245 eV) which is still more intense and less blue-shifted for clusters, compared to the multilayer spectrum, and (ii) in the region around 250 eV. Differences in energy scales between the solid and cluster spectra are discounted since both spectra were brought to a common energy scale, according to our energy calibration using atomic argon as an energy reference. Pavlychev *et al.* have

pointed out, according to theoretical work, that the regime around 250 eV is sensitive to the local environment of excited atoms (21). Similar findings are reported by Björneholm *et al.* from experiments on free argon clusters (19).

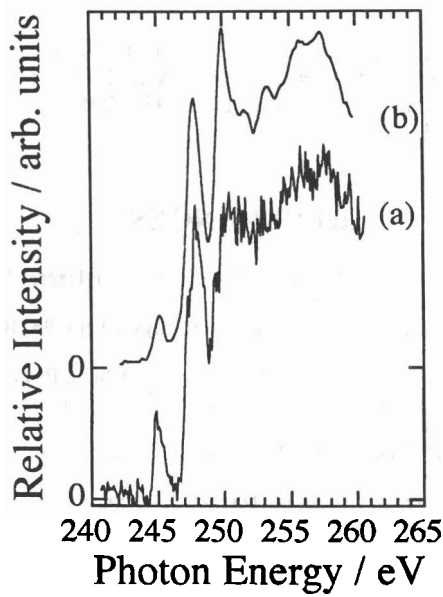

Figure 4. (a) Auger electron yield spectrum of argon clusters ($\overline{N}$=530) where a contribution of 40% of the atomic component has been subtracted; (b) Auger electron yield for thick multilayers of argon (adapted from ref. (21)).

These differences in shape are likely related to the dominant contribution of the surface of the clusters to the Auger electron yields as compared to the condensed phase. Argon microclusters are known to have polyicosahedral structures, in contrast to the fcc lattice of the solid (14). According to estimates by Hoare, one expects for six closed icosahedral shells, corresponding to Ar_{561}, that 45% of the atoms are located on the surface of the cluster (23). The smaller blue-shift of the 4s-exciton, compared to the multilayer spectrum, is therefore an indication that primarily the surface atoms contribute to the Auger yield of microclusters. Further experiments with improved spectral resolution using undulators in conjunction with high resolution x-ray monochromators are proposed in order to confirm this result.

Conclusions

The results indicate that Auger electron yields of variable size argon clusters are highly sensitive to the environment of the excited atom within a cluster. The intensities of the near-edge features indicate that Auger electrons originate primarily from the surface of clusters rather than from the bulk. This shows that Auger

yields of free clusters are a valuable complement to investigations of the direct photoionization process studied by ZEKE photoelectron spectroscopy, as well as total electron yield spectroscopy where intense inelastic scattering is used as a probe of bulk properties of clusters.

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