Neighbor-induced photoelectron recapture in argon clusters: A photon-energy-dependent study of Auger spectra

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A photon-energy-dependent experimental study of the $L_{2,3}M_{2,3}M_{2,3}$ Auger transitions in argon clusters is presented, and features without atomic counterparts are observed in the spectra up to photon energies at least 30 eV above the $L_{2,3}$ threshold. We propose that these features are due to the process of neighbor-induced recapture, in which the outgoing photoelectron is backscattered by neighboring atoms in the cluster, loses energy in a Bremsstrahlung-like inverse photoemission process, and is recaptured in a Rydberg orbital of the core-ionized atom before Auger decay.

Ionic final states, except the lowest, undergo relaxation after a photoionization process. Radiative decay may be the only energetically allowed relaxation process for valence ionized states, but for core hole states (c^{-1}), radiationless Auger decay is also possible, leading to two-hole states, for instance in the valence level (v^{-2}), and two outgoing electrons: the photoelectron and the Auger electron. At low excess energies, these two electrons interact, resulting in the slow photoelectron losing kinetic energy and the fast Auger electron gaining it. Close to the threshold, the photoelectron can lose all its kinetic energy and be recaptured to produce a state with two valence holes and the recaptured electron in a Rydberg orbital $(v^{-2}R)$ (see Refs. [1–5]).

In this paper we present an experimental study of $2p$ Auger decay in argon clusters, which at photon energies above the $2p$ threshold exhibit extra spectral features present in neither the well-understood atomic spectra nor the cluster spectra recorded high above threshold. The data show similarities to the atomic postcollision-interaction- (PCI-) induced recapture process, but also significant differences. Possible mechanisms for this are discussed; we propose an explanation of the observation. This is a process in which the outgoing photoelectron is backscattered by neighboring atoms in the cluster, loses its energy in a Bremsstrahlung-like inverse photoemission process [6], and is recaptured in a Rydberg orbital of the core-ionized atom before the Auger decay. We expect the proposed mechanism to be of importance also for other nonconducting systems.

Argon clusters were produced with a supersonic expansion source, with the mean size $\langle N \rangle$ of 3700 [7]. Details of the experiment are found elsewhere [8]. In this work the argon $L_{2,3}M_{2,3}M_{2,3}$ Auger transitions were studied. The measurements were performed at the Swedish synchrotron radiation facility MAX-lab at beamline I411, using a Scienta R4000 electron spectrometer placed at the magic angle relative to the plane of the linearly polarized radiation. The total resolution in the spectra was 70 meV.

In Fig. 1 three spectra of the Ar *LMM* region are pre-

sented. The spectra were recorded with different photon energies $h\nu=258$ eV, about 10 eV above the $L_{2,3}$ threshold, which sets the photoelectron kinetic energy below the argon cluster second ionization, exciton, and shake-up thresholds (≈ 13 eV); $h\nu=280$ eV, an intermediate data point above the second ionization threshold but below the L_1 threshold; and finally, $h\nu=360$ eV, above the L_1 threshold. The atomic spectrum consists of five lines ($^3P_{2,1,0}, {}^1D_2, {}^1S_0$) from each of the spin-orbit split core-ionized components, which were used for energy calibration [9].

Far above threshold, as in the 360 eV spectrum, it is possible to decompose the Ar *LMM* Auger cluster signal into surface and bulk contributions [8] by using broadened versions of the atomic signal [9], shifted due to the polarization screening [10]. The energy shifts for the cluster components in the Auger spectra, indicated in Fig. 1(a), are well predicted using the surface and bulk shifts determined from an x-ray photoelectron spectroscopy (XPS) spectrum [8]. The surface fraction of the total cluster intensity, obtained from the fit in Fig. 1(a), was 0.60. The fit includes a linear background accounting for effects due to photoelectron inelastic scattering leading to secondary ionization in the clusters. As seen in Fig. 1, the background becomes less pronounced as the photon energy is decreased. This is due to the changed probability of secondary ionization, as discussed in detail in Ref. [11]. In conclusion, both the atomic and high-photon-energy cluster Auger spectra are well understood.

The kinetic energy of the Auger electrons is set by the relative position of the energy levels involved in the decay and the second ionization potential. Hence, a changed photon energy should not alter the kinetic energy position of the Auger signal in either the atomic or the cluster case except through PCI near the threshold. However, in Fig. 1 large photon-energy-dependent intensity changes are observed, especially in the higher-kinetic-energy part of the spectra. As the photon energy is decreased from $h\nu=360$ to 258 eV, we observe an apparent energy shift toward higher kinetic energy of the cluster bulk peak at about 207 eV. In the high-kinetic-energy end of Fig. 1(c), around 211 eV, features with no correspondence in Fig. 1(a) are observed. By then comparing to the spectrum in Fig. 1(b), recorded using the photon energy 280 eV, we observe that the additional features are found at constant kinetic energy, and do not disperse with the photon energy.

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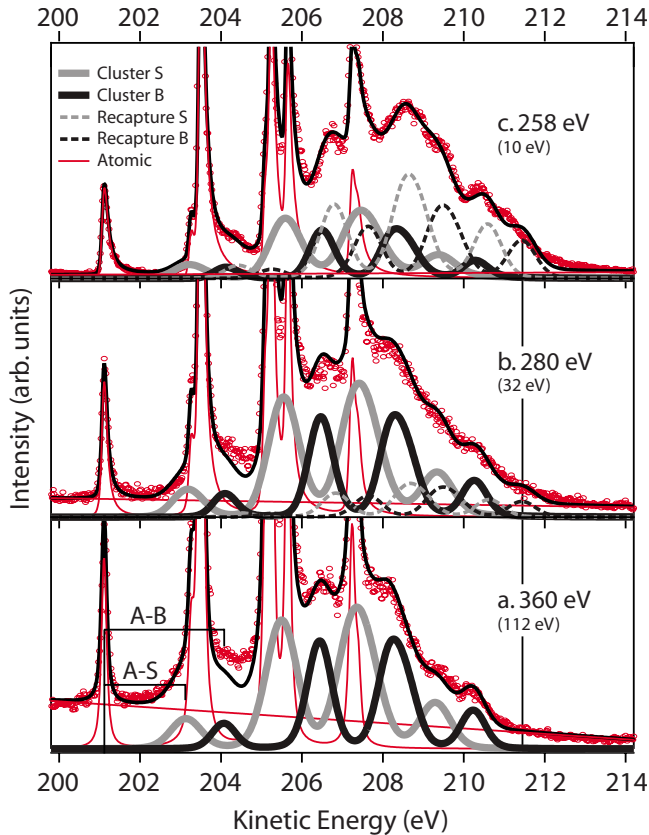
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FIG. 1. (Color online) Cluster ($\langle N \rangle$=3700) spectra of the Ar *LMM* Auger transition region for three different photon energies. Curve fits are included with assignment of intensity due to the cluster surface (S) and bulk (B) as well as intensity due to photoelectron recapture in the cluster surface and bulk. The atom-surface (A-S) and atom-bulk (A-B) shifts are indicated in the spectrum for $h\nu$ =360 eV (a). The line at ~211.5 eV is intended to illustrate the highest kinetic energy where intensity is found in the spectrum for $h\nu$=258 eV (c). The numbers in parentheses give the approximate kinetic energies of the ejected photoelectrons in each case.

In a recent study of decay processes just above the $3d$ threshold in free Kr clusters, nondispersing Auger-like features were observed at higher kinetic energies than expected [12]. The origin of these features was discussed in terms of excitation of the photoelectron into the delocalized conduction band just above the core-ionization threshold. The Auger electron would in this case gain kinetic energy due to the lower charge resulting from the presence of the photoelectron still in the vicinity of the decaying core hole in the cluster. Assuming the photoelectron to be in a shell with a radius equal to that of the cluster, R, which would minimize the electrostatic repulsion, the Auger electron would gain approximately $1/R$ in kinetic energy as it passes the photoelectron, due to the change in effective charge of the ion. Though simple, this PCI-like model's qualitative prediction that this shift in Auger energy should depend inversely upon the cluster radius (i.e., cluster size) is reliable. In the case studied here the photon energy is much farther above the ionization threshold, which makes excitation into the delocalized conduction band less likely. Furthermore, we cannot observe any strong dependence on size for the high-kinetic-

energy features presented in Ref. [11] when going from mean sizes of 60 to 2100 atoms (see Fig. 5 of [11]), or indeed this study, where the mean size is estimated to be 3700 atoms. According to the model used in Ref. [12], the $1/R$ dependence of the shift would result in a change of the shift with a factor of $(3700/60)^{1/3} \approx 4$ for the Auger electron, and this is clearly not observed. Thus, excitation of the photoelectron into the conduction band does not explain the presence of the high-kinetic-energy Auger features.

The highest-kinetic-energy features in the well-understood 360eV spectrum reflect the energy difference between the initial $2p_{1/2}^{-1}$ state and the final lowest localized $3p^{-2}$ state [8]—independent of excitation energy. In order for features to appear at higher kinetic energy, an energy increase of the initial and/or an energy decrease of the final state must occur. A possible photon-energy-dependent process that could affect the initial state is electronic excitation in the photoionization event [13], such as shake-ups or excitons. These processes require at least 13 eV excess energy, i.e., more than the 10 eV excess energy available in the case of the lowest photon energy (258 eV). Changes of the initial state as a cause for the features at higher kinetic energy may therefore be excluded.

The final-state energy may be affected by several processes. One possibility is secondary, extra-atomic ionization by the photoelectron. This can be excluded since the lowest-photon-energy measurement yields photoelectrons with kinetic energies lower than the exciton and ionization thresholds. Another possibility for lowering the energy is delocalization of the two final-state holes. The resulting lowering of the final-state energy (causing the increase of the Auger kinetic energy) would depend on how spatially separated the valence holes are. The minimum value, about 9 eV, would stem from two holes localized on neighboring atoms [twice the first ionization potential (IP) with a Coulomb repulsion term subtracted from the sum of the first and second IPs in argon clusters]. This minimum energy increase is much larger than what is observed in the spectra—furthermore, no intensity has been observed in the region about 9 eV and above the normal Auger energy region.

Electrons from the decay of neutral core-excited states with similar higher kinetic energy than in normal Auger processes have been observed in resonant Auger spectra, where an electron occupies a high Rydberg orbital after resonant excitation ($c^{-1}R$) [14]. The photon energy bandwidth used was, however, sufficiently narrow to exclude accidental resonant features in our spectra. Still, the cluster environment offers mechanisms that neutralize the core-ionized atom by placing an electron in a bound Rydberg state, e.g., via charge transfer from a neighbor. This is, however, energetically forbidden in argon solids since the IP of the electron-donating atom is about 13 eV, while the neutralization offers at most a 3 eV relaxation (the difference between a $2p^{-1}$ and a $2p^{-1}4s$ state [14]).

Another electron, released upon a secondary ionization by the photoelectron could also be captured, creating the $c^{-1}R$ state. This can be excluded since the photoelectron kinetic energy (10 eV) is below the IP (13 eV) in the 258 eV experiment. The only remaining option involves a recombination of the photoelectron and the ion.
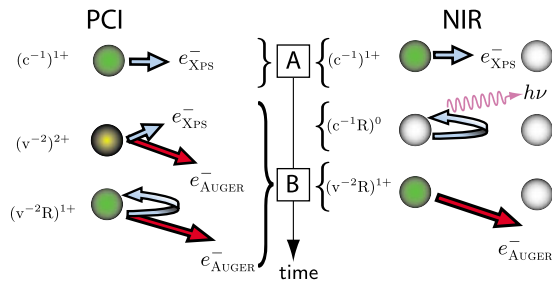
FIG. 2. (Color online) Schematic of the PCI-induced recapture and normal Auger processes (left) and the neighbor-induced recapture process (right). c represents core, v, valence, R, Rydberg, and the superscripts show the electron configuration and state charge. The time scale shows the photoionization event (A) and the Auger decay (B).

In atomic argon the recombination process is well studied [1,3,4]. Here the process, called recapture, is related to the PCI between the photoelectron and Auger electron (see the left side of Fig. 2). The probability of this PCI-induced atomic recapture process decreases rapidly with increasing photoelectron kinetic energy, and is negligible already at 3 eV in the Ar atomic case [2,5]. The recapture phenomenon observed here differs from the PCI-related recapture, since the kinetic energy of our photoelectrons is too large (>10 eV) for PCI-induced recapture to play an important role. Furthermore, in the atomic recapture process the total energy is retained in the system by giving the Auger electron additional kinetic energy corresponding to the photoelectron kinetic energy, i.e., after recapture the Auger electron kinetic energy will disperse with photon energy. In the cluster spectra, in contrast to the above, the observed high-kinetic-energy features do not disperse with photon energy, and we may conclude that, if the recapture process is occurring in the clusters, it must include a way for the outgoing photoelectron to lose its kinetic energy.

Above we have ruled out electronic excitation as such a loss mechanism. Another possibility is phonon creation, which would be directly detectable as energy loss features in the XPS (as well as valence spectra). No such intensity related to energy loss has been observed below excess energies of 13 eV.

Since both these loss mechanisms can be excluded, the remaining option for energy loss for a 10 eV photoelectron in the argon cluster is emission of radiation in a Bremsstrahlunglike process. This process is the base for the investigative technique *inverse photoemission* [6]—where the excess energy (the difference between the electron kinetic energy and the Rydberg orbital binding energy) is emitted as a photon. Investigations of solid Xe using inverse photoemission have been performed using electrons with 10–25 eV kinetic energy [15]. We propose that this is the energy loss mechanism present in our experiment on argon clusters, as illustrated on the right side of Fig. 2. This would yield a constant higher kinetic energy of the Auger electron since the energy of the initial state is increased more than the final state's by the recapture of an electron into a Rydberg state. The high-kinetic-energy features observed in the Auger spectra are the signature of the decay from this excited state. To underline

the distinction from PCI-induced recapture we call this process, depicted on the right side of Fig. 2, neighbor-induced recapture (NIR). This is a local recapture process, compatible with the observed lack of any size dependence.

Inverse photoemission is usually not a strong process, but an important difference between the standard measurements of neutral films and our case is that there is an ion in our system. The fact that there is a positive charge in the cluster may increase the cross section for inverse photoemission [16], and we propose that the proximity of the ion and the photoelectron immediately after the photoemission makes the process even more probable.

Investigations using electrons for ionization of free Ar atoms show that PCI-related recapture of a slow electron after the interaction leads to additional structures on the high-kinetic-energy side of the Auger LMM signal [17]. At low excess energies an intense feature is found at 1.4 eV above atomic features on the kinetic energy scale. The curve fit included in Fig. 1(a) shows that the cluster bulk and surface lines at highest kinetic energy are at about 210.2 and 209.3 eV, respectively. In the curve fit of the close to threshold ($h\nu=258$ eV) spectrum we have used the energy positions of the cluster surface and bulk features found in the 360 eV measurement and introduced two more sets of peaks, accounting for recapture intensity in the surface and bulk. PCI line shapes were used for both the atomic [18] and cluster normal Auger features [19]. The peaks describing the cluster normal Auger features have fixed intensities relative to the atomic parent lines. In the surface and bulk recapture peaks the relative intensity was not fixed to the atomic reference, to allow for variations in the recapture probability between the two spin-orbit components, due to their different kinetic energies. However, the individual multiplets internally retained the same relative intensities as in the atomic Auger spectrum, and the surface and bulk recapture features were given the same relative intensities. The shape of the recapture features is complex. The energy distribution of the Rydberg orbitals involved in the recapture process could perhaps suggest the use of an asymmetric line shape to model the recapture signal but due to the lack of knowledge about this issue we have assumed a simple Gaussian line shape. In Fig. 1(c) the resulting curve fit is displayed. Here we have allowed the energy position and width of the Gaussian recapture features to be free. The curve fit accounts for most of the recapture intensity, and the deviations are ascribed to the imperfection of using a Gaussian line shape.

The surface signal fraction of the normal Auger cluster features in the fit of the $h\nu=258$ eV case was 0.62. The kinetic energy shift of the recapture features was about 1.25 eV for both the surface and bulk features, i.e., slightly smaller than the maximum shift observed in the atomic case. From the fitting procedure, we find that approximately half of the total cluster specific intensity in the spectrum is NIR related at 258 eV photon energy. For the $h\nu=280$ eV measurement, i.e., with the photoelectron kinetic energy above the ionization threshold, the curve fit found the same energy positions of the recapture features as in the $h\nu=258$ eV case, within the experimental accuracy. The surface signal fraction was found to be 0.60 in the normal Auger features, similar to the previously mentioned cases. Here, we find that a fifth of

the total cluster specific intensity is due to the NIR process. This intensity decrease reflects the decreasing recapture probability with increasing kinetic energy of the photoelectron. Close to threshold, PCI-induced recapture should compete with NIR. The two processes will populate the same final states, and will therefore be indistinguishable in the electron spectrum. In a classical picture, the time it takes for an electron to be backscattered from the nearest neighbor with as low energy as 0.1 eV is less than the core-hole lifetime, which could be an indication that NIR may occur even at such a low energy.

From the low-resolution spectra presented in Ref. [11], it is clear that the relative intensity of the features we attribute to this recapture process is lower for the $\langle N \rangle = 60$ clusters than for the $\langle N \rangle = 2100$ clusters. This indicates that the process is more likely in the bulk of the clusters. In Fig. 1, the surface fraction of the total cluster intensity is higher for the regular Auger features than for the features due to recapture (0.62 and 0.59, respectively, at 258 eV; 0.60 and 0.53, respectively, at 280 eV), consistent with a larger probability of the process to occur in the bulk.

In conclusion, we propose that neighbor-induced recapture of the photoelectron has high probability far above the $L_{2,3}$ ionization threshold in Ar clusters: at 10 eV above threshold around half of the cluster intensity in the Ar *LMM* region is related to the recapture process. At about 30 eV above threshold a fifth of the cluster intensity is still associated with this process.

The NIR process should be a general phenomenon occurring in systems with nonmetallic screening, such as insulators and semiconductors. As discussed above, the NIR process involves an inverse-photoemission-like conservation of energy. We would like to encourage experimental work observing the fluorescence of this process.

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