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Anomalously strong shake-up processes in Auger decay of the resonantly excited $2p^5 3s^2 3p^6 nl$ states of Ar

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The $2p$ electrons of Ar have been excited selectively to the $2p^5 3s^2 3p^6 nl$ ($nl = 4s, 5s, 3d, 4d$) states by synchrotron radiation. The resulting Auger-like spectra have been measured for the first time with high resolution and analyzed in detail. The structures in the experimental spectra have been identified by comparing the experimental Auger energy shifts due to various nl spectator electrons with the corresponding calculated values. Anomalously high intensities have been found for the transitions corresponding to simultaneous shake up of the spectator electron.

INTRODUCTION

In recent studies of Auger decay processes of resonantly excited Kr and Xe atoms, the peaks corresponding to shake-up processes of the spectator electron showed[1-3] high intensities, up to 30% of the main peaks. In this paper we will present the first high-resolution $2p$ resonance Auger spectra for Ar and interpret them by comparison with calculated values. The spectra of Ar are important for studies of systematic trends, especially the role of shake up, in the resonance Auger spectra of the rare gases Xe, Kr, and Ar. For the first time, we show that shake-up intensity can be even greater than the primary intensity.

A high shake-off probability for the first resonances of Kr and Xe was recently observed experimentally.[4,5] The calculations reported by Heimann *et al.*[5] predicted a high total shake probability. The values contained the shake-up contribution as well, which accounted for nearly the total shake probability. This prediction was not, however, confirmed experimentally.

The absorption and electron energy-loss[6] spectra as well as multiply charged ion spectra[7] in the vicinity of the $2p$ threshold of Ar show strong peaks below the ionization threshold corresponding to excitations of $2p$ electrons to empty $4s$, $5s$, $3d$, and $4d$ states. Several of these states are, however, energetically close or overlapping. The best separated is the $2p_{3/2} \rightarrow 4s$ excitation at 244.4 eV. The transitions $2p_{3/2} \rightarrow 5s$ and $2p_{3/2} \rightarrow 3d$ at 246.9 eV overlap completely and also the $2p_{1/2} \rightarrow 4s$ is very close on their low-energy side (246.5 eV). Again the $2p_{3/2} \rightarrow 6s$ and $2p_{3/2} \rightarrow 4d$ excitations overlap at 247.8 eV as well as the $2p_{3/2} \rightarrow 7s$ and $2p_{3/2} \rightarrow 5d$ at 248.3 eV just below the $2p_{3/2}$ ionization threshold. Studies of the $2p_{1/2}$ excitations are difficult due to the fact that the strongest resonance excitation peak $2p_{1/2} \rightarrow 3d$ is already above the $2p_{3/2}$ ionization threshold.

The low cross sections for the selective excitations of Ar $2p$ electrons and the relatively high photon and electron energies make the measurements of Ar $2p$ resonance Auger spectra rather difficult. So far as we know this is the first high-resolution report on these measurements which have been possible due to the high photon flux from our beam line.

For intensity reasons we have used a rather broad photon bandwidth (~1 eV, 0.2 Å). The resonance Auger spectra were taken at photon energies 244.4 eV covering the isolated $2p_{3/2} \rightarrow 4s$ excitation [Fig. 1(a)]; 246.5 eV covering the $2p_{1/2} \rightarrow 4s$ and $2p_{3/2} \rightarrow 3d, 5s$ excitations [Fig. 1(b)]; 247.5 eV covering both the $2p_{3/2} \rightarrow 3d, 5s$ and $2p_{3/2} \rightarrow 4d, 6s$ excitations [Fig. 1(c)]; and 249.7 eV that was adjusted to create $2p_{3/2}$ normal Auger spectrum superposed by the $2p_{1/2} \rightarrow 3d, 5s$ excitation [Fig. 1(d)].

RESULTS AND DISCUSSION

The experimental measurements were carried out by using the Canadian Synchrotron Radiation Facility at the 1 GeV Aladdin storage ring in Stoughton, Wisconsin, and a Leybold-Heraeus LHS-11 electron spectrometer.[8]

Figure 1 displays the energy region of the $L_{2,3}M_{2,3}M_{2,3}$ Auger line group of Ar obtained using (a) 244.4-, (b) 246.5-, (c) 247.5-, and (d) 249.7-eV photons to excite or ionize the $2p$ levels. The excited states may decay with the excited electron as the spectator or the participator. The final states for the participator processes are single-hole states where one electron is removed from an orbital. These states can also be reached through the ordinary photoemission process. The $3s$ photoline in Figs. 1(a)–1(d) is, however, considerably weaker than the other structure indicating that the excited states do not significantly decay via the $3s$ participating process. In separate measurements only slight variations were observed in the partial cross section for $3s$ and $3p$ ionizations thus showing that the excited states mainly decay by the spectator Auger process. This is in agreement with earlier

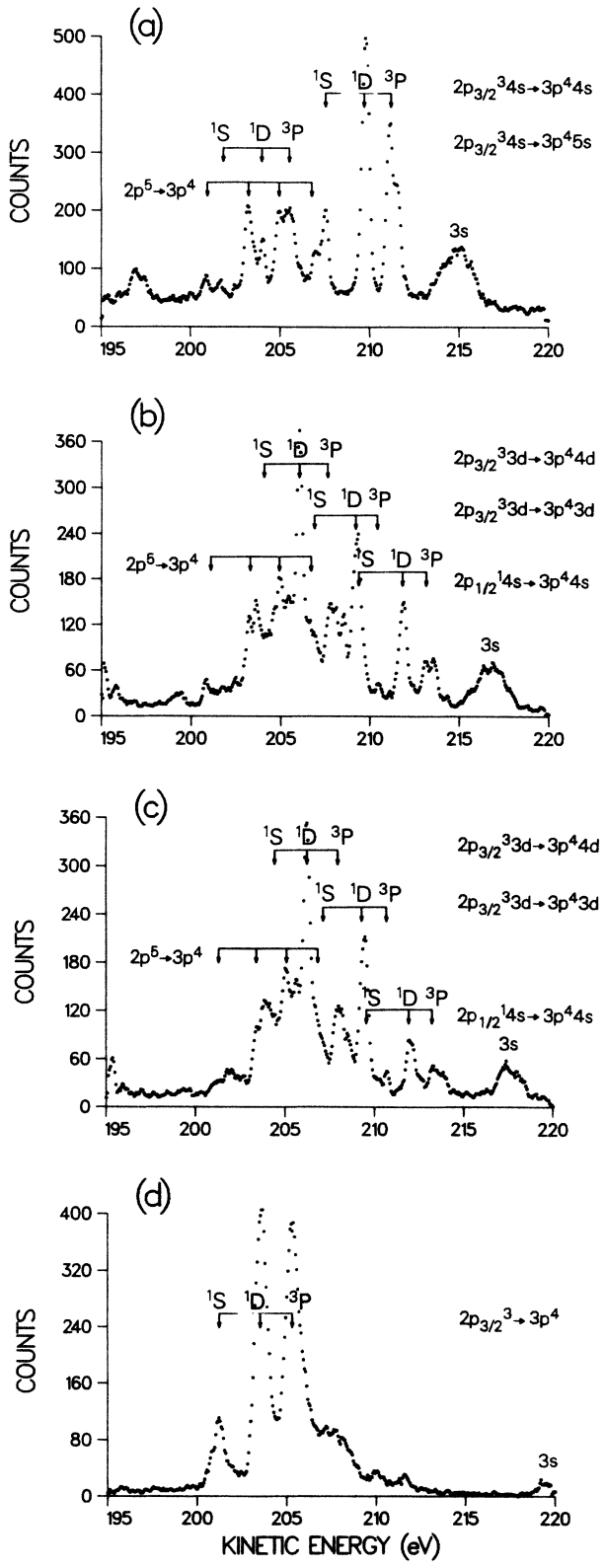

FIG. 1. Resonance Auger spectra of Ar recorded using (a) 244.4-, (b) 246.5-, and (c) 247.5-eV photons to excite the $2p$ electrons to the Rydberg states. (d) displays the $L_3M_{2,3}M_{2,3}$ spectrum after ionization of the $2p_{3/2}$ level by 249.7-eV photons. Slight smoothing has caused some artificial structure especially in $3s$ photoelectron lines.

findings for Kr and Xe (Refs. 1 and 2).

The photon energy of 244.4 eV causes only the $2p_{3/2} \rightarrow 4s$ excitations, which is well separated ($\sim$2 eV) from other resonances. The main structure in the spectrum [Fig. 1(a)] is due to the $2p_{3/2}^3 4s \rightarrow 3p^4 4s$ Auger decay with a $4s$ spectator electron. These "$4s$ spectator Auger lines" have shifted 6.6 eV to higher kinetic energies from the corresponding normal $2p_{3/2}^3 \rightarrow 3p^4$ Auger peaks[9] [compare Figs. 1(a) and 1(d)]. The theoretical value of 6.37 eV obtained with the use of the MCDF (multiconfiguration Dirac-Fock) code[10] agrees well with the experimental value. Extra structure on the low-energy side is mainly due to the normal $2p^5 \rightarrow 3p^4$ Auger transitions originating from ionization by second- and higher-order diffracted light and by scattered light in the photon beam. The normal-Auger spectrum is, furthermore, accompanied on its high-energy side by a weak spectrum that is found to be shifted by about 0.8 eV from the normal spectrum. According to the MCDF calculations, the $2p_{3/2}^3 4s \rightarrow 3p^4 5s$ decay, where a shake up of the spectator electron takes place during the Auger decay, should fall 0.97 eV to higher energies from the normal spectrum. This good agreement between the experimental and calculated energy shifts and the lack of other excitation possibilities at this photon energy enables us to assign these peaks to the $2p_{3/2}^3 4s \rightarrow 3p^4 5s$ decay. The finding is analogous with the previous observations in the corresponding spectra of Kr and Xe.[1,2] A least-squares fit of the spectrum using the computer code CRUNCH[11] yields the branching ratio of 5.0 for the $(2p_{3/2}^3 4s \rightarrow 3p^4 4s)/(2p_{3/2}^3 4s \rightarrow 3p^4 5s)$ intensity ratio.

Figure 1(b), where the 246.5-eV photons are used for the excitation, shows a more complicated spectral structure. At this photon energy and applied photon bandwidth three excitations, $2p_{1/2} \rightarrow 4s$ at 246.5 eV, $2p_{3/2} \rightarrow 3d$ and $2p_{3/2} \rightarrow 5s$ at 246.9 eV, are possible and result in three different spectator Auger transitions. The $2p_{1/2}^1 4s \rightarrow 3p^4 4s$ decay gives highest kinetic energies. These peaks have found to be shifted by 8.6 eV experimentally and by 8.50 eV theoretically from the normal $2p_{3/2}^3 \rightarrow 3p^4$ spectrum. The energy shift of 5.72 eV was obtained for the $2p_{3/2}^3 3d \rightarrow 3p^4 3d$ decay theoretically and 6.0 eV experimentally. The calculations predict a shift of 3.27 eV for the $2p_{3/2}^3 5s \rightarrow 3p^4 5s$ decay, but experiment does not show any clear structure at this position, which is also in agreement with the absorption results.[6,7] On the other hand, a very strong spectrum shifted by 2.8 eV from the $2p_{3/2}^3 \rightarrow 3p^4$ spectrum shows up. The calculated energy shift of 2.60 eV for the $2p_{3/2}^3 3d \rightarrow 3p^4 4d$ decay agrees well with this experimental finding, which strongly suggests that the origin of the structure is the $3d \rightarrow 4d$ shake up of the spectator electron during the Auger decay. This shake up is an exceptionally strong process. A branching ratio of 0.8 is observed for the $[2p_{3/2}^3 3d \rightarrow 3p^4(^1D)3d]/[2p_{3/2}^3 3d \rightarrow 3p^4(^1D)4d]$ intensity ratio.

The spectra shown in Fig. 1(c) seem to agree with those of Fig. 1(b), even though the intensities are somewhat different. The 247.5-eV photon energy used in Fig. 1(c) to create the spectrum should give more strength to the processes with the spectator electron in higher Rydberg orbitals. Thus the lines due to the $2p_{3/2} \rightarrow 3d,5s$ and

$2p_{3/2} \rightarrow 4d,6s$ excitations should increase relative to the lines due to the $2p_{1/2} \rightarrow 4s$. In fact, the structure due to the $2p_{1/2} \rightarrow 4s$ excitation has relatively decreased to the half from the previous spectrum. Otherwise, the spectrum has not changed significantly. The strong $3d \rightarrow 4d$ shake-up spectrum overlapping with the spectrum due to the decay of the $2p_{3/2} \rightarrow 4d$ excitations, dominates again in the profile.

The $2p_{3/2}^3 \rightarrow 3p^4$ spectrum is shown in Fig. 1(d). The ionization of the $2p_{3/2}$ level is possible at 249.7 eV mean photon energy but the energies still lie below the $2p_{1/2}$ ionization threshold. Weak structure at the high-energy side is due to the spectator Auger decay of excited $2p_{1/2}$ states with the excited electron at high ($3d,5s$ and $4d,6s$) Rydberg orbital. Also the photoabsorption results[7] show that transitions to these Rydberg states form weak peaks on high continuum absorption background.

Shake off during the Auger decay was observed by Becker *et al.*[4] to be a very strong decay channel in the resonance Auger spectra of Xe. The same was found very recently for Ar, Kr, and Xe by Heimann *et al.*[5] Our finding now indicates that the shake-up decay probability is of the same order as shake off. Shake up is also found to be much more pronounced in cases where the excited electron is a $3d$ electron instead of a $4s$ electron. The finding indicates an extremely delocalized, diffuse character of the $3d$ Rydberg state, allowing such an Rydberg electron to hop into the next Rydberg state during the Auger process. According to the recent theoretical predictions,[5] based on the use of overlap integrals between the Rydberg orbital before Auger-like decay and higher Rydberg orbitals afterwards, shake up would be an extremely strong decay channel. Our high-resolution results accompanied with detailed interpretation of the fine-structure peaks, confirm the importance of the shake up during the Auger-like decay of the excited state. This is especially true for the $3d$ excited orbital of Ar. The upper part of Fig. 2 displays the wave functions of the $3d$(Ar), $3d(Ar^+)$, and $4d(Ar^+)$ orbitals. The $3d$(Ar) and $4d(Ar^+)$ functions are strongly overlapping. The overlap is not so pronounced for the $4s$(Ar) and $5s(Ar^+)$ wave functions depicted in lower part of Fig. 2. The squares of the overlap integrals of the $3d$(Ar) and $4d(Ar^+)$ functions and of the $4s$(Ar) and $5s(Ar^+)$ functions were found to be 0.63 and 0.12, respectively. The collapse of the $3d$ orbital is thus responsible for the observed strong shake-up probability. The $3d$ orbital collapse in going from the initial $2p_{3/2}^3 3d$ state to the final $3p^4 3d$ state makes it likely that the Rydberg electron will simultaneously go to the next orbital. On the basis of an independent-particle shake picture, the observed behavior can be understood qualitatively, even though more sophisticated theoretical predictions are needed for a detailed description.

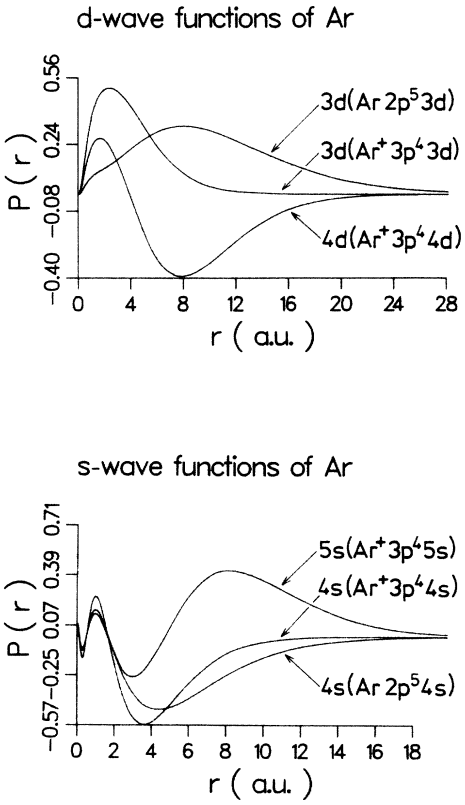

FIG. 2. Radial wave functions of Ar Rydberg orbitals in the initial and final states of Auger-like decay.

CONCLUSIONS

High-resolution $2p$ resonance Auger spectra of Ar have been measured for the first time and the spectra have been analyzed in detail by comparing with theoretical calculations. Besides the expected structures, very intense peaks have been observed which are proposed to originate from shake-up processes of the spectator electrons during the Auger-like emission.

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