Multiplet-dependent shake-up structures in high-resolution Auger spectra at $3d^{-1}4s^24p^6np, n=5,6$ resonances of Kr

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Shake-up transitions during the Auger decay of the Kr $3d^{-1}np$, $n=5,6$ resonance states have been studied with high photon and electron resolution (<0.1 eV) using the Aladdin undulator beamline in Stoughton, Wisconsin. This resolution enables us to resolve the complex spectra and study the distribution of intensity between the multiplets of the $4p^{-2}np$ final states. The intensity distribution between these multiplets has been found to depend strongly on the principal quantum number n, and theoretical intensity calculations are in good agreement with experiment. Correspondingly, shake fractions differ for each parent and also depend strongly on whether the electron is excited to the first or second Rydberg orbital.

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INTRODUCTION

In their pioneering work, Eberhardt, Kalkoffen, and Kunz first presented the Auger spectrum of atomic Kr at the $3d \rightarrow 5p$ resonance [1]. The spectrum exhibited "spectator" resonance Auger lines ($3d^94s^24p^65p \rightarrow 3d^{10}4s^24p^{-2}5p$ transitions) accompanied by shake-up transitions, $3d^94s^24p^65p \rightarrow 3d^{10}4s^24p^{-2}6p$. The spectator Auger spectrum shifts to higher kinetic energy from the normal Auger spectrum and, in addition, shake transitions take place during the Auger decay.

In the past six years, these spectra, and the analogous Xe $3d$ and Ar $2p$ spectra, have been studied extensively both experimentally and theoretically [2–10]. However, with the exception of some high-resolution threshold electron spectra [4,5], the electron resolution of normally ≥ 0.25 eV was not sufficient to resolve the detailed multiplet structure of spectator and shake transitions. In addition, the photon resolutions for generally ≥ 0.3 eV often made it impossible to avoid exciting more than one resonance transition leading to even more complicated overlapping resonance Auger spectra. For example, because the energies of the Kr $3d_{5/2} \rightarrow 6p$ and $3d_{3/2} \rightarrow 5p$ transitions differ only by ~ 0.1 eV, only very complicated overlapping Auger spectra have been observed for these two transitions. Theoretical analysis and assignment of the peaks have been very difficult because of these problems. Simplifying assumptions (such as the intensity distributions in normal, spectator, and shake-up spectra are the same) had to be made. However, in recent relatively high-resolution Ar $2p \rightarrow 3d$ resonance Auger spectra, a redistribution of intensity has been noted [10].

Recently, with high-resolution monochromatized synchrotron radiation from undulator [11] and bending magnet [12,13] beamlines at Aladdin, we have been able to obtain high-quality core-level photoelectron spectra rapidly with photon and electron resolution of <0.1 eV. In this paper, we use this high resolution to reinvestigate the Kr $3d$ resonance Auger spectra. The increased resolution, together with theoretical calculations, enables a more confident assignment, and in particular highlights details of intensity redistribution which have not been previously considered.

EXPERIMENT AND THEORY

The spectra presented here were obtained using a high-resolution photoelectron spectrometer at the pseudo-magic-angle [14]. The resolving power of the analyzer ($\Delta E/E$) for 1-mm slits is $\sim \frac{1}{720}$. For kinetic energies of ~ 60 eV in this study, we obtain an electron resolution for ~ 80 meV. Photons from the undulator on the Aladdin storage ring were monochromatized using a 2400-groove/mm grating in a 6-m toroidal grating monochromator with an excitation bandwidth of <90 meV at 100 eV [15] photon energy. Spectra of high-purity Kr (99.99%) were obtained between 51 and 65 eV kinetic energies at the energies for the excitations $3d_{5/2} \rightarrow 5p$ (91.2 eV), $3d_{3/2} \rightarrow 5p$ (92.4 eV) [Figs. 1(a) and 1(b)], and $3d_{5/2} \rightarrow 6p$ (92.5 eV), $3d_{3/2} \rightarrow 6p$ (93.8 eV) [Figures 2(a) and 2(b)]. Spectra were fitted to Lorentzian-Gaussian line shapes.

The calculations were made by factorizing the Auger amplitudes into products of two elements. The first element, related to monopole shake up, was obtained by overlap integrals of the orbital of the shaking electron before and after Auger decay. The second element, corresponding to the Auger decay induced by the two-electron operator, was computed using a package originally formulated to predict the single-channel Auger transitions in open shell atoms by taking intermediate coupling and configuration interaction into account [2]. The same

Auger integrals as in Ref. [16] were used also in this work. The population of the initial states in excitation was predicted with the GRASP code of Grant and coworkers [17]. Furthermore, the eigenvalues and eigenvectors of the $4p^{-2}np$ states were obtained by taking the interaction with the configurations $4s^{-2}np$ and $4p^{-1}np^{-1}$ into account using the GRASP code. The calculated energies were not, however, in a good agreement with the experiment indicating that configuration interaction was treated inadequately. The eigenvectors may thus also be somewhat inaccurate resulting in errors in intensity predictions. Channel interaction was not taken into account in this work. This may also be one source for the discrepancy between calculated and experimental relative intensities.

RESULTS AND DISCUSSION

The experimental spectra are shown in Figs. 1 and 2. The assignment of the different transitions is shown in the upper part of the figures. Detailed assignment and the calculated relative intensities (experimental and theoretical) are also given in Tables I and II for the spectra in Fig. 1.

The peak widths in all the spectra are ~0.14 eV, very close to that expected based on the 0.10-eV Kr $3d$ natural linewidth [18] and the electron resolution for 0.08 eV. This resolution enable resolution of many peaks not resolved on previous spectra. Also, the high photon resolution enables clean $3d_{3/2} \rightarrow 5p$ and $3d_{5/2} \rightarrow 6p$ resonance Auger spectra. For example, the $^1D(7p)$ peak in Fig. 2(a) at 54.74 eV is barely noticeable in Fig. 1(b). Conversely, the intense $^1D(5p)$ peak at 59.44 eV in Fig. 1(b) is not noticeable in Fig. 2(a). Also, there is no sign of "normal" Auger peaks [19] from second-order radiation. The undulator was tuned to first order at ~90 eV, and there is no appreciable second-order excited Auger spectra from off-resonance spectra at 180 eV photon energies.

The calculated relative intensities and ratios in Tables I and II are in fairly good agreement with experiment. The assignments of multiplets given in Tables I and II are similar to those given by Carlson, Lindle, and Grimm [7] on the basis of optical data. Due to the strong mixing of several LS states, the LS coupling scheme is not well suited to assign the states and therefore only the J values should be considered as reliable.

Both theoretical and experimental results show a redistribution of intensities. For example, the ratio of $^1S:^1D:^3P$ was predicted to be 1:3.2:1.6 in the spectator and 1:2.7:1.8 in the shake-up spectrum of the $3d_{5/2}^{-1}5p$ state. Experimentally, the respective ratios are 1:2.7:1.5 and 1:2.1:2.0, in reasonable agreement with theory, and *very* different for the ratios in the normal Auger electron spectrum of 1:1.4:1.2.

The eigenvectors obtained in the energy calculations

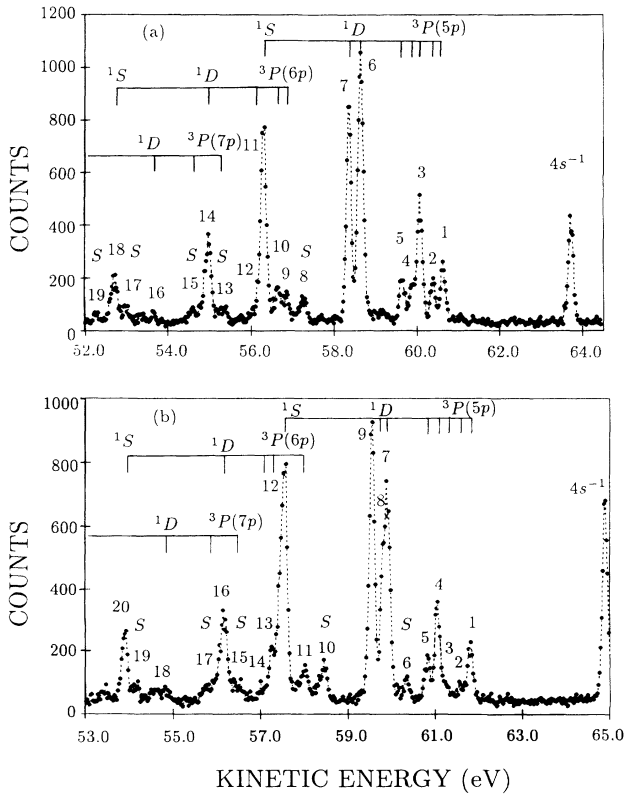

FIG. 1. Resonance auger spectra of Kr after exciting: (a) the Kr $3d_{5/2}$ electron and (b) the Kr $3d_{3/2}$ electron to the $5p$ Rydberg states at 91.2 and 92.4 eV, respectively.

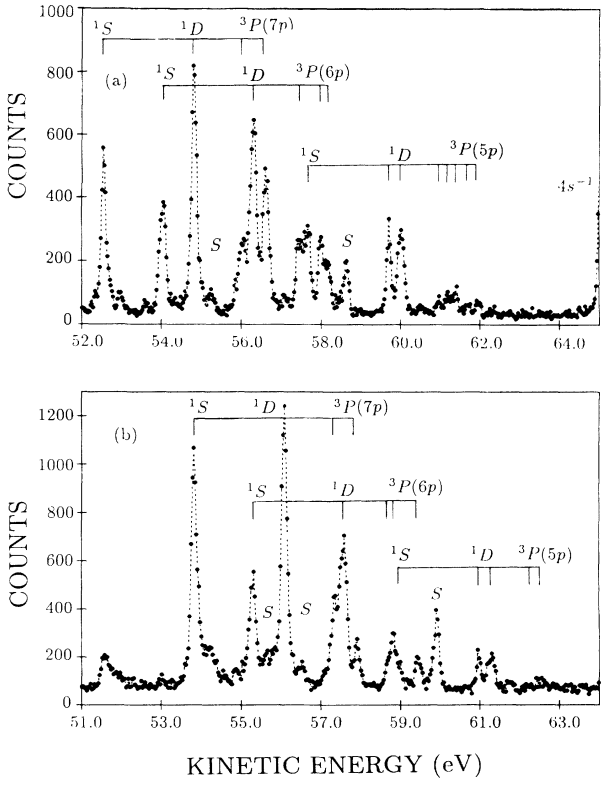

FIG. 2. Resonance Auger spectra of Kr after exciting: (a) the Kr $3d_{5/2}$ electron and (b) the Kr $3d_{3/2}$ electron to the $6p$ Rydberg states at 92.5 and 93.8 eV, respectively. The Kr $4s$ "satellites" are denoted S.

TABLE I. Energies and intensities of the transitions at the $3d_{5/2}^{-1}5p$ resonance.

Peak in Fig. 1(a)	Assignment of the final state	Energy (eV) Expt.	Energy (eV) Calc.	Intensity (%[a]) Expt.	Intensity (%[a]) Calc.
1	$(^3P)5p(^4P_{3/2,5/2})$	60.52	60.94,61.00	4.4	4.6
2	$(^3P)5p(^4P_{1/2},^4D_{5/2,7/2})$	60.28	60.74,60.72,60.77	3.0	3.6
3	$(^3P)5p(^4D_{3/2})$	59.97	60.40	9.5	6.6
4	$(^3P)5p(^2P_{1/2},^4D_{5/2},^2P_{1/2,3/2})$	59.78	60.29,60.24,60.22,60.18	3.0	4.2
5	$(^3P)5p(^4S_{3/2},^4D_{3/2},^2S_{1/2})$	59.54	60.02,59.91,59.87	3.3	3.5
6	$(^1D)5p(^2F_{5/2,7/2},^2P_{3/2})$	58.54	58.76,58.70,58.48	24.0	29.9
7	$(^1D)5p(^2D_{3/2,5/2},^2P_{1/2})$	58.26	58.19,58.33,58.36	16.3	13.8
8	4s sat. $[(^1D)4d]$[b]	57.13		2.3	
9	$(^3P)6p$	56.75	57.3	1.8	2.1
10	$(^3P)6p$	56.54	57.2	3.0	2.2
11	$(^1S)5p(^2P_{1/2,3/2})$	56.20	56.75,56.74	15.2	13.6
12	$(^3P)6p$	56.12	56.7	3.5	2.5
13	$(^3P)7p$ and/or 4s sat. $[(^1S)4d]$[b]	55.21		1.2	
14	$(^1D)6p$	54.87	55.2	8.7	10.0
15	$(^3P)7p$ and/or 4s sat. $[(^1D)5d]$[b]	54.59		2.3	
16	$(^1D)7p$	53.55		0.7	
17	4s sat. $[(^1D)6d]$[b]	52.89		1.4	
18	$(^1S)6p$	52.59	53.4	4.1	3.7
19	4s sat. $[(^1D)7d]$[b]	52.16		0.7	

[a]As percentages from the sum for the $3d_{5/2}^{-1}5p \rightarrow 4p^{-2}5p$ and $3d_{5/2}^{-1}5p \rightarrow 4p^{-2}6p$ transitions.
[b]From Ref. [20].

clearly showed a strong mixing of some parents. For example, the $(^3P)np(^4D_{3/2})$, $(^3P)np(^2P_{3/2})$, $(^1D)np(^2P_{3/2})$, and $(^1D)np(^2D_{3/2})$ states were found to be heavily mixed, the strength of the mixing depending on the principal quantum number n. This explains the sensitivity of relative intensities to n. This also gives rise to the large differences in shake to spectator ratios (Table III) if obtained for each parent multiplet separately. Single-channel calculations reproduce nicely the observed sensitivity in the branching ratio of parent multiplets even though the relative intensities are not fully reproduced.

Thus, in addition to the energy shift and the splitting of the levels due to the coupling with the spectator electron [2–10], the intensity for the parent multiplets is also redistributed in going from the normal Auger to the resonance spectra. Thus the picture that the resonance spec-

TABLE II. Energies and intensities of the transitions at the $3d_{3/2}^{-1}5p$ resonance.

Peak in Fig. 1(b)	Assignment of the final state	Energy (eV) Expt.	Energy (eV) Calc.	Intensity (%[a]) Expt.	Intensity (%[a]) Calc.
1	$(^3P)5p(^4P_{3/2,5/2})$	61.70	62.15,62.22	3.9	4.6
2	$(^3P)5p(^4P_{1/2},^4D_{5/2,7/2})$	61.48	61.95,61.92,61.99	1	1.2
3	$(^3P)5p(^4D_{3/2})$	61.09	61.61	2.0	1.1
4	$(^3P)5p(^2P_{1/2},^4D_{5/2},^2P_{1/2,3/2})$	60.94	61.50,61.47,61.44,61.40	6.0	6.1
5	$(^3P)5p(^4S_{3/2},^4D_{3/2},^2S_{1/2})$	60.72	61.22,61.13,61.11	2.9	5.5
6	4s sat. $[(^1S)5s]$	60.24		1.3	
7	$(^1D)5p(^2F_{5/2,7/2})$	59.80	59.97,59.91	16.8	13.0
8	$(^1D)5p(^2P_{3/2})$	59.68	59.69	4.7	2.4
9	$(^1D)5p(^2P_{1/2},^2D_{3/2,5/2})$	59.44	59.40,59.55,59.58	20.4	26.9
10	4s sat. $[(^1D)4d]$	58.32		3.3	
11	$(^3P)6p$	57.88	58.6	3.5	0.5
12	$(^1S)5p(^2P_{1/2,3/2})$	57.45	57.96,57.95	17.7	18.5
13	$(^3P)6p$	57.38	58.4	4.0	0.9
14	$(^3P)6p$	57.16	58.0	4.0	3.1
15	$(^3P)7p$ and/or 4s sat. $[(^1S)4d]$	56.36		3.5	
16	$(^1D)6p$	56.05	56.4	7.3	11.0
17	$(^3P)7p$ and/or 4s sat. $[(^1D)5d]$	55.77		3.6	
18	$(^1D)7p$	54.74		0.8	
19	4s sat. $[(^1D)6d]$	54.04		1.0	
20	$(^1S)6p$	53.78	54.6	5.6	5.1

[a]As percentages from the sum of the $3d_{3/2}^{-1}5p \rightarrow 4p^{-2}5p$ and $3d_{3/2}{}^{-1}5p \rightarrow 4p^{-2}6p$ transitions.

TABLE III. Branching ratios between shake and spectator transitions.

Initial state	Ratio	^1S Calc.	^1S Expt.	^1D Calc.	^1D Expt.	^3P Calc.	^3P Expt.	Total Calc.	Total Expt.
$3d_{5/2}^{-1}5p$	$I(6p)/I(5p)$	0.27	0.27±0.05	0.23	0.22±0.03	0.31	0.36±0.15	0.26	0.27
$3d_{3/2}^{-1}5p$	$I(6p)/I(5p)$	0.27	0.32±0.09	0.26	0.17±0.02	0.25		0.26	
$3d_{5/2}^{-1}6p$	$I(5p)/I(6p)$	0.19		0.21		0.24		0.22	
$3d_{5/2}^{-1}6p$	$I(7p)/I(6p)$	1.54	1.46±0.15	1.40	1.30±0.15	1.68		1.51	
$3d_{3/2}^{-1}6p$	$I(5p)/I(6p)$	0.21	0.14±0.06	0.21	0.42±0.07	0.25		0.22	
$3d_{3/2}^{-1}6p$	$I(7p)/I(6p)$	1.54	1.67±0.25	1.49	1.39±0.25	1.52	1.60±0.25	1.51	

trum is only shifted does not hold true. Due to the low resolution in previous experiments, the change of intensity was not observed earlier. High resolution is thus needed to be able to make complete conclusions from the data.

Furthermore, the intensity ratio of multiplets is also different in spectator and shake-up spectra. This has interesting consequences. The ratio of shake-up to spectator processes is 0.27 (theory gives 0.26, Table III) when obtained from the sum of the multiplets. However, for each parent multiplet, the ratio differs considerably from that. The branching ratios are given in Table III for all the spectra shown in Figs. 1 and 2. They were obtained from the fitted results analogous to those presented for the spectra of Fig. 1 in Tables I and II. Inspection of Table III shows that if only the strongest peaks are considered when obtaining the branching ratio as usually done, the results would be misleading.

Angular distribution of Auger electrons [7] is usually obtained by referencing to one of the multiplets. Since the shake contribution differs for each multiplet, the procedure may be a source of inaccuracy. Since the shake probabilities often are very high (e.g., $6p \rightarrow 7p$), reliable results must include shake processes when angular distributions are considered.

Parent mixing caused by the $4p$-np interaction is found to alter the intensity distribution considerably in case of the resonance Auger decay of Kr. Similar effects are expected to be present in general. High resolution is, however, necessary to bring them into sight.

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