Shake processes in the Auger decay of resonantly excited $3d^9 4s^2 4p^6 np$ states of Kr

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The spectra of Auger-like electrons of Kr have been studied in detail in the photon energy range of the $3d_{3/2}$ and $3d_{5/2} \rightarrow np$ ($n = 5,6,7,8$) excitations. In addition to the $3d^{-1}np \rightarrow 4p^{-2}np$ spectator Auger-like lines the spectra show structures where the spectator electron is shaken up or down during the decay. Their contribution is found to increase in going to the excitations to higher Rydberg orbitals. Shake calculations are found to agree fairly well with the observed shake contributions.

I. INTRODUCTION

The decay of the $3d_{3/2,5/2} \rightarrow 5p$ resonance states of Kr has been studied recently in Refs. 1–7. The spectator-electron picture has been used successfully to explain the main spectral structures of the inner-shell discrete decay processes. The nonspectator autoionization decay can also occur for the inner-shell resonances, but it has been found to be usually much less intense than the spectator decay.[3,4] A very remarkable probability for a process where the spectator electron jumps to a next Rydberg orbital has also been observed. Especially in the case of Ar $2p \rightarrow 3d$ excitaion, the $3d \rightarrow 4d$ shake-up was found to be a very strong decay channel in a recent study.[8] On the other hand, shake-off probability was found[5,9] to increase in Ar, Kr, and Xe resonance spectra with increasing n. The calculations of Heimann *et al.*[5] predicted high total shake probability for the monopole shake transitions. It was almost solely done by the shake-up component, but this was not, however, confirmed experimentally.[5]

The ion yield measurements[10] for Kr have shown a minor production of Kr^+ at first resonances, whereas Kr^{2+} was found to be the dominant product of these resonant decay processes. Furthermore, the production of doubly and triply charged ions was found to increase with n. For the most important pathway to double-charged ions, Hayaishi *et al.*[10] proposed a two-step Auger-like decay, whereas a shake-off of the spectator electron was favored by Heimann *et al.*[5]

As an attempt to clarify the situation concerning the relative roles of different shake processes in the decay of the highly excited states, we have carried out a detailed comparison between calculated monopole shake-up or -down probabilities and experimental high-resolution measurements.

II. EXPERIMENT

The experiment was carried out at the Hamburger-Synchrotron-Strahlungslabor HASY-LAB at Deutsches Elektronen-Synchrotron DESY using the 5.6-m toroidal grating monochromator.[11] The bandpass of the mono-

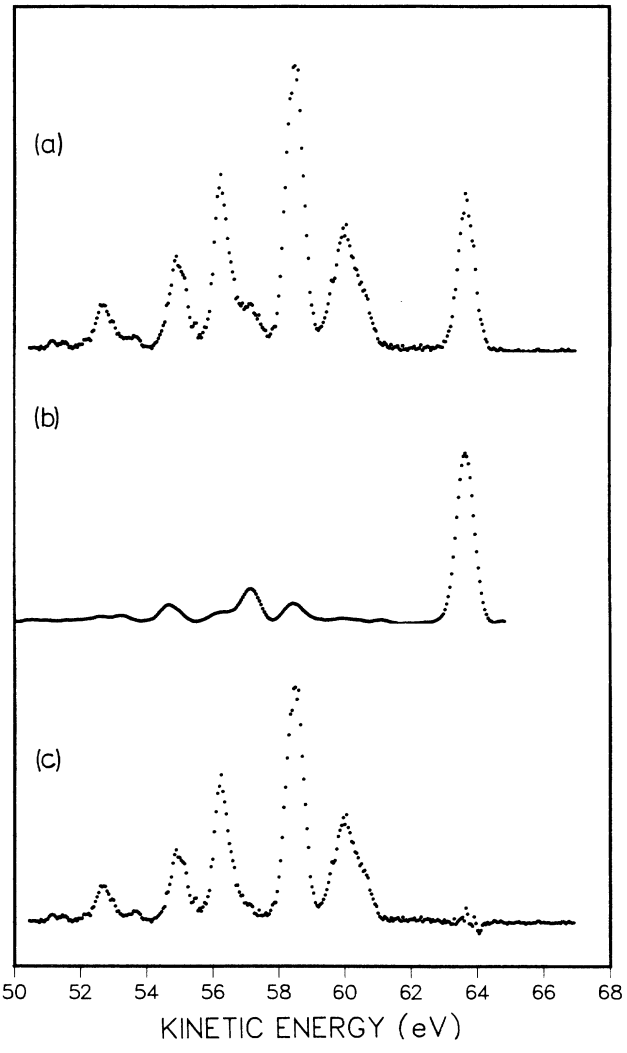

FIG. 1. (a) Electron spectrum of Kr after the $3d_{5/2} \rightarrow 5p$ resonance excitation. (b) 4s photoelectron spectrum of Kr. (c) The spectrum (a) after the subtraction of the spectrum (b). The fit of this spectrum is depicted in Fig. 2(a).

chromatized light was less than 0.35 eV at $h\nu=91.2$ eV. The spectra were measured with a cylindrical mirror-type analyzer.[12] The energy resolution of the spectrometer was 0.78% from the pass energy of the electrons. Most spectra were taken without the preretardation. The experimental results are shown in Figs. 1–3. Figure 2 shows the kinetic energy region of 50–64 eV of the ejected electron spectra of Kr after excitation of the $3d_{5/2}$ electron to the $5p$, $7p$, and $8p$ Rydberg states at 91.2, 93.0, and 93.3 eV photon energies.[13] Figure 3, furthermore, displays the spectra after excitation of the $3d_{3/2}$ electrons at 92.5, 93.8, and 94.3 eV photon energies. The photon energy of 92.5 eV used for the $3d_{3/2}\rightarrow 5p$ excitation is also able to excite the $3d_{5/2}$ electron to an empty $6p$ level due to a very small energy separation[13] in the excitation energies. The $3d_{3/2}\rightarrow 6p$ and $3d_{3/2}\rightarrow 7p$ excitations take place at 93.8 and 94.3 eV.

Besides the resonant excitations the used photons cause significantly also the direct photoemission of the $4s$ electrons. At the resonance excitation energies the $4s$ photoline also includes the transition where the excited electron participates in the Auger process. Its relative contribution is small however.[4] The relatively high strength of the direct $4s$ photoemission makes the subtraction of the $4s$ satellite lines, which overlap energetically with the resonance lines, from the spectra very important. In the applied subtraction procedure it is supposed that the satellite structure of the $4s$ photolines remains unchanged also at the resonant photon energies. For the subtraction, the $4s$ photoelectron spectrum was carefully measured at nonresonant photon energies of 90 and 91.8 eV. In order to keep the statistics of the difference spectrum reasonable and to adjust the linewidths the photoelectron spectrum was slightly smoothed. The scaled and smoothed spectrum [Fig. 1(b)] was then subtracted from the resonantly excited spectra as demonstrated in Fig. 1.

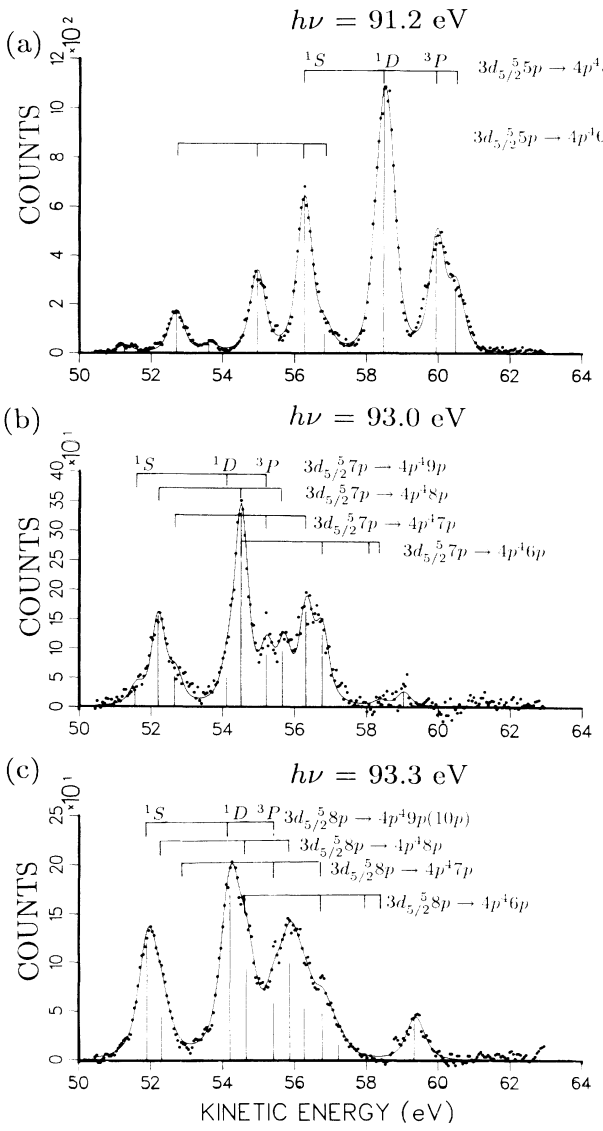

FIG. 2. Ejected electron spectra of Kr taken at photon energies of 91.2, 93.0, and 93.3 eV. Solid curves and vertical lines represent least-squares fits of Voigth functions to the data points. For notations see the text.

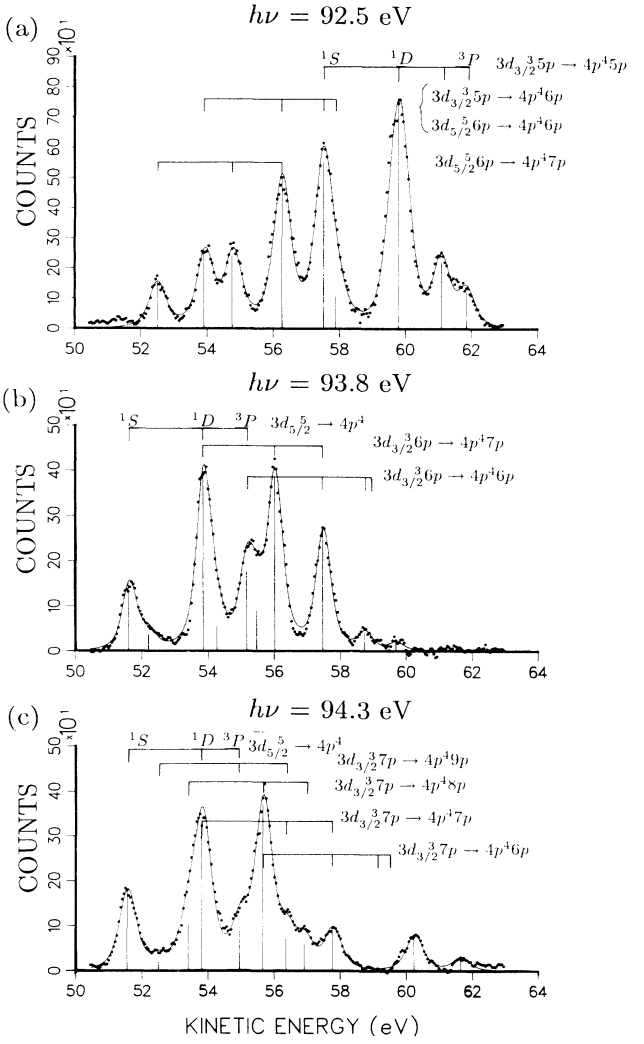

FIG. 3. Ejected electron spectra of Kr taken at photon energies of 92.5, 93.8, and 94.3 eV.

III. DISCUSSION

A. Interpretation of the experiment

The spectra taken at 91.2 and 92.5 eV photon energies have been observed and analyzed in detail previously.[2,4] The spectra were found to be mainly due to the Auger-like transitions $3d^{9}_{3/2,5/2}5p \rightarrow 4p^{4}5p$ with the $5p$ electron as a spectator. The $5p \rightarrow 6p$ shake-up of the spectator electron during the decay and resulting in an extra structure in the spectra was estimated to be 20–30 % from the intensity of the main decay process where the $5p$ electron remains in the $5p$ orbital. A least-squares fitting of present high-resolution results gives a shake-up contribution of (22±5)% (of the total shake-up plus spectator probability) in the case of the $3d^{-1}_{5/2}5p$ spectrum, for which the shake-up contribution can be determined fairly accurately. The value was obtained with the aid of the $(^1S)np$, $(^1D)np$, and $(^3P)np$ lines [see Fig. 2(a)] after estimating the ratio of the overlapping $(^1S)5p$ and $(^3P)6p$ lines so that the ^1S to ^1D ratio was the same in both spectra. Different widths of the Voigth functions were used in the fit in order to take into account that the lines are composed of several fine-structure lines due to the coupling with the np electron. The inaccuracy of 5% thus arises from both of the above-told approximations in the data handling.

The partition of the decay of the $3d^{-1}_{3/2}5p$ state to spectator and shake-up channels from the experimental spectrum is more difficult due to the overlap of the $3d_{3/2} \rightarrow 5p$

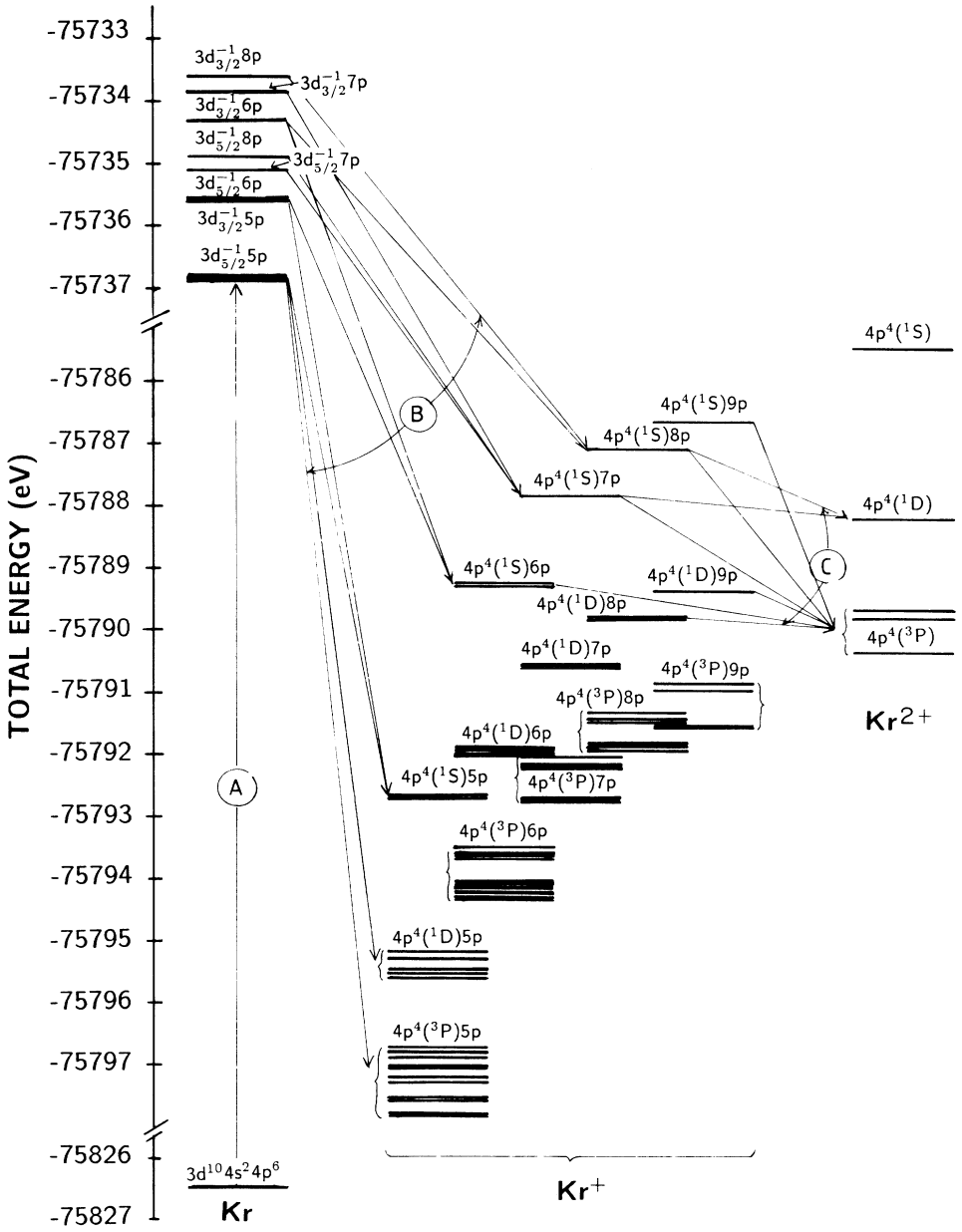

FIG. 4. Energy-level diagram of Kr predicted with the MCDF calculations.

and $3d_{5/2} \rightarrow 6p$ excitations [Fig. 3(a)]. However, by recording a series of spectra with photon energies ranging from 92.3 to 92.75 eV, it has been possible to approximately resolve from the spectra the contributions of the two excitations because the spectrum due to the $3d_{3/2} \rightarrow 5p$ excitation dominates at 92.3 eV photon energy whereas the spectrum due to the $3d_{5/2} \rightarrow 6p$ dominates at 92.75 eV. The shake-up contribution of (25±5)% has been obtained for the $3d_{3/2}^{-1}5p$ spectrum in good agreement with the $3d_{5/2}^{-1}5p$ spectrum.

The spectra taken at the resonances with the $3d$ electron excited to higher Rydberg states show many-fold structures analogously with the spectrum at the first resonance. If the spectra were done by the spectator transitions alone, we should see only three peaks due to the transitions to the $4p^4(^1S)np$, $4p^4(^1D)np$, and $4p^4(^3P)np$ final states since the open shell splitting is decreasing with $n \geq 7$ according to the energy calculations (see Fig. 4). Instead we see structures due to several overlapping lines. This clearly indicates that shake-up or -down processes play a strong role also in these spectra. In order to be able to identify the individual lines in the experimental spectra, Dirac-Fock calculations[14] for the energy levels were performed. Figure 4 shows the calculated energy-level diagram. Calculated energies, obtained by taking the difference between the initial- and final-state energies, were used to identify different decay modes in the experimental spectra. The difference between calculated and experimental energies was allowed to vary 0–0.3 eV since theory overestimates also the normal Auger $3d^{-1} \rightarrow 4p^{-2}(^1D)$ energies by 0.2 eV. The interpretation of the peaks given in Figs. 2–3 was thus obtained. The calculated and experimental kinetic energies are given in Table I. The energies are the mean values of the fine structures of the $3d^{-1}np \rightarrow 4p^{-2}(^1D)np$ transitions. Since the fine-structure splitting [e.g., $4p^4(^1D)np$, $J = \frac{1}{2}, \frac{3}{2}, \frac{3}{2}, \frac{5}{2}, \frac{5}{2}, \frac{7}{2}$] is not resolved in experiment, only one Voigth function was used to determine the energy position of the $3d^{-1}np \rightarrow 4p^{-2}(^1D)np$ transitions. Furthermore, based on the least-squares fit of the experimental spectra, the partition of the total decay intensity into spectator, shake-up, and shake-down components was carried out. These results are given in Table II.

The partition of the observed intensity to spectator, shake-up, and shake-down contributions was done by using the intensities only of the ^1S and ^1D components because the intensity of the ^3P was too low to be resolved, and it was often strongly overlapping with other lines. The last two factors cause some inaccuracy into the given numbers of Table II, and therefore the numbers should not be taken too literally. The tendency is clear, however, and shows the transfer of the intensity from the spectator to the shake spectra with increasing n.

The spectator spectrum seems to decrease in going from the first resonance excitation to the higher excitations (see also Figs. 2 and 3). Most striking are the spectra of Figs. 2(b), 2(c), and 3(c), where the energies of 93.0, 93.3, and 94.3 eV were used to cause the excitations $3d_{5/2} \rightarrow 7p$, $3d_{5/2} \rightarrow 8p$, and $3d_{3/2} \rightarrow 7p$, respectively. On the basis of a comparison with calculated energies, it is obvious that the spectator Auger-like decay is of minor importance in experimental spectra. In addition to the structures due to shake-up, the high kinetic energy side displays extra peaks that fit fairly well energetically with the shake-down processes. Due to the small energy separation in the photon energies between the spectra at $3d_{5/2} \rightarrow 7p$ and $3d_{5/2} \rightarrow 8p$ excitations [Figs. 2(b) and 2(c)], the decay processes of former excitation may also contribute to the latter one.

With the aid of the measured kinetic energies (Table I) and used photon energies we also determined the binding energies of the $4p^4(^1D)np$ states to be 32.7, 36.3, 37.8,

TABLE I. Calculated and experimental energies in eV.

Transition		Energy		
Initial state	Final state	Calculated	Experimental	$h\nu$
$3d_{5/2}^{-1}5p$	$4p^{-2}(^1D)5p$	58.54	58.5	91.2
$3d_{5/2}^{-1}5p$	$4p^{-2}(^1D)6p$	55.19	55.1	91.2
$3d_{5/2}^{-1}6p$	$4p^{-2}(^1D)6p$	56.45	56.3	92.5
$3d_{5/2}^{-1}6p$	$4p^{-2}(^1D)7p$	55.02	54.8	92.5
$3d_{5/2}^{-1}7p$	$4p^{-2}(^1D)6p$	56.93	56.8	93.0
$3d_{5/2}^{-1}7p$	$4p^{-2}(^1D)7p$	55.50	55.2	93.0
$3d_{5/2}^{-1}7p$	$4p^{-2}(^1D)8p$	54.76	54.5	93.0
$3d_{5/2}^{-1}7p$	$4p^{-2}(^1D)9p$	54.32	54.1	93.0
$3d_{5/2}^{-1}8p$	$4p^{-2}(^1D)6p$	57.17	56.8	93.3
$3d_{5/2}^{-1}8p$	$4p^{-2}(^1D)7p$	55.74	55.4	93.3
$3d_{5/2}^{-1}8p$	$4p^{-2}(^1D)8p$	55.00	54.7	93.3
$3d_{5/2}^{-1}8p$	$4p^{-2}(^1D)9p$	54.55	54.2	93.3
$3d_{5/2}^{-1}8p$	$4p^{-2}(^1D)10p$	54.28		
$3d_{3/2}^{-1}5p$	$4p^{-2}(^1D)5p$	59.77	59.8	92.5
$3d_{3/2}^{-1}5p$	$4p^{-2}(^1D)6p$	56.42	56.3	92.5
$3d_{3/2}^{-1}6p$	$4p^{-2}(^1D)6p$	57.68	57.5	93.8
$3d_{3/2}^{-1}6p$	$4p^{-2}(^1D)7p$	56.26	56.0	93.8
$3d_{3/2}^{-1}7p$	$4p^{-2}(^1D)6p$	58.16	57.8	94.3
$3d_{3/2}^{-1}7p$	$4p^{-2}(^1D)7p$	56.74	56.4	94.3
$3d_{3/2}^{-1}7p$	$4p^{-2}(^1D)8p$	56.00	55.7	94.3

TABLE II. Calculated and experimental relative shake probabilities.

Transition		Shake Probability		
			Experimental	
Initial state	Final state	Calculated	M_4	M_5
$3d^{-1}5p$	$4p^{-2}5p$	0.793	0.75	0.78
$3d^{-1}5p$	$4p^{-2}6p$	0.205	0.25	0.22
$3d^{-1}5p$	$4p^{-2}7p$	0.001		
$3d^{-1}5p$	$4p^{-2}np/\epsilon p$	0.000		
$3d^{-1}6p$	$4p^{-2}5p$	0.079		
$3d^{-1}6p$	$4p^{-2}6p$	0.364	0.39	0.32
$3d^{-1}6p$	$4p^{-2}7p$	0.549	0.61	0.68
$3d^{-1}6p$	$4p^{-2}8p$	0.007		
$3d^{-1}6p$	$4p^{-2}np/\epsilon p$	0.005		
$3d^{-1}7p$	$4p^{-2}5p$	0.105		
$3d^{-1}7p$	$4p^{-2}6p$	0.024	0.19	0.23
$3d^{-1}7p$	$4p^{-2}7p$	0.048	0.11	0.17
$3d^{-1}7p$	$4p^{-2}8p$	0.731	0.62	0.50
$3d^{-1}7p$	$4p^{-2}9p$	0.091	0.09	0.10
$3d^{-1}7p$	$4p^{-2}np/\epsilon p$	0.001		
$3d^{-1}8p$	$4p^{-2}6p$	0.045		0.13
$3d^{-1}8p$	$4p^{-2}7p$	0.040		0.16
$3d^{-1}8p$	$4p^{-2}8p$	0.017		0.25
$3d^{-1}8p$	$4p^{-2}9p$	0.583		0.46
$3d^{-1}8p$	$4p^{-2}10p$	0.297		
$3d^{-1}8p$	$4p^{-2}np/\epsilon p$	0.018		

38.6, and 39.1 eV for $n=5$, 6, 7, 8, and 9, respectively. Calculated $4p^4(^1D)np$ ($n=5$, 6, 7, 8, and 9) binding energies of 31.2, 34.6, 36.0, 36.7, and 37.2 eV deviate from experiment by 1.5–1.9 eV. A difference of 1.8 eV was also found between the calculated (38.4 eV) and experimental[15] (40.2 eV) binding energies of the $4p^4(^1D)$ state. The $4p^4(^1D)5p$ binding energy of 32.75 eV determined in a photoelectron study by Svensson *et al*[16] agrees well with our experimental value. They[16] also reported the line at 36.47 eV to be due to the $4p^4(^1D)5d$ and $4p^4(^1D)6p$ states and the line at 37.81 eV to contain besides the $4p^4(^1D)6d$ state also the $4p^4(^1D)7p$ state. Our results confirm the assignments of the above-mentioned lines.

The photon energy of 93.8 eV is just above the ionization limit for the $3d_{5/2}$ electron. The spectrum in Fig. 3(b) thus contains a contribution due to the $3d^3_{5/2}\rightarrow 4p^4$ normal Auger decay. It was found to be shifted by about 0.25 eV due to the post-collision interaction (PCI). A PCI shift of 0.2 eV was observed with 94.3-eV photons [Fig. 3(c)].

B. Comparison with shake calculations

In order to find theoretical estimates for the shake-up probabilities, we calculated the overlap integrals between the Rydberg orbital before Auger-like decay and higher Rydberg orbitals afterwards. The wave functions of the Rydberg orbitals were obtained with the Dirac-Fock calculations using the multiconfiguration Dirac-Fock (MCDF) computer code of Grant *et al.*[14] The calculated values of the shake probabilities are given in Table II. The calculated shake probability seems to increase with n, the excited electron being shaken up to the next Rydberg orbital as well as to the next one over. Also the shake-down probability starts to become important when n increases. The calculations show that in going to higher excitations, the collapse of the np wave function is increasing, and the overlap with the $(n+1)p$ and $(n+2)p$ orbitals becomes stronger, the second maximum of np also overlapping with $(n-1)p$. Figure 5 displays the radial wave functions of Kr Rydberg orbitals before and after the Auger-like decay of the $3d^97p$ excited state.

So far we have considered only the transitions with $4p^{-2}np$ final states. The spectrum taken at photon energy of 92.60 eV by Lindle *et al.* (Fig. 1 in Ref. 4) shows prominent peaks 4 and 7, the first one of which is due to the $3d^3_{5/2}6p\rightarrow 4s^14p^5(^1P)7p$ decay and the second one to its correlation satellite $4s^24p^34d7p$ according to our energy analysis. This indicates that the shake-up processes are of the same importance for Auger-like transitions

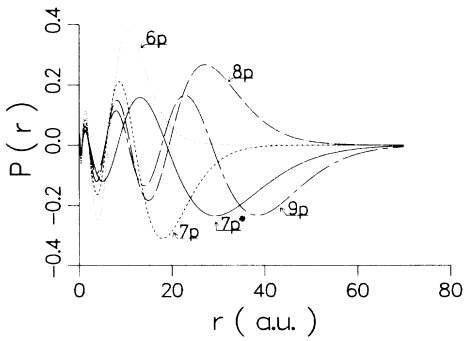

FIG. 5. Radial wave functions of Rydberg orbitals of Kr. $7p^*$ stands for the initial state $3d^97p$ and np ($n=6,7,8,9$) for the final state $4p^4np$.

with $4p^4np$ or $4s^14p^5np$ final states. Our preliminary calculations also gave about the same shake probabilities to the transitions with both of these final states. The overlap integrals were found to be rather insensitive to the coupling of the ionic core.

Results of this work based on a comparison between experiment and simple shake theory show that the shake-up of the *np* electron to the next Rydberg orbital or the next one over or even shake-down occur very likely during the Auger-like decay of the $3d^{-1}np$ ($n=5,6,7,8$) excited states. Especially the $3d^{-1}\rightarrow 4p^{-2}$ transitions, studied now in very detail, are almost solely done by the spectator and shake-up or -down transitions. Therefore the two-step process (steps *B* and *C* in Fig. 4) may play a prominent role in the formation of the doubly charged ions. Inspection of the energy-level diagram (Fig. 4) also shows that in the case of higher excitations, second-step decays *C* for larger number of final states of first step *B* become energetically possible. Thus the $4p^4(^1S)np(n=6,7,8,9)\rightarrow 4p^4(^3P)$ decay is possible, as well as the $4p^4(^1D)np(n=8,9)\rightarrow 4p^4(^3P)$ decay. Also the $4p^4(^1S)np(n=7,8,9)$ states lie above the $4p^4(^1D)$ state, allowing the second-step Auger process. Energies of all the transitions *C* fall at the kinetic energy region of 0–4 eV. Therefore the intensity is expected to peak more sharply around 0 eV at higher *np* resonances, as observed by Heimann *et al.* (Fig. 8 in Ref. 5).

Simple shake theory reproduces the shake structure at 50–64 eV kinetic energy fairly well. The low kinetic energy region of the spectrum is, however, more difficult to be analyzed due to several reasons: The correlation satellites accompanying the 4*s* hole states (e.g., $4s^04p^6np$ and $4s^14p^5np$), due to the interaction $4s^{-1}\leftrightarrow 4s^{+1}4p^{-2}n'd$ ($n'=4,5,\ldots,\epsilon$), are present. Electron correlation is very sensitive to the degree of the ionization and to the states of other electrons in atom. Therefore variation in the strength and distribution of the correlation satellites are expected at excitations to different Rydberg orbitals. Because of the large number of energy levels created in the first step due to correlation effects, a great number of second-step transitions are expected and thus several overlapping peaks appear at the low kinetic energy region. High-resolution measurements, complemented with detailed theoretical analysis, are neeeded to distinguish peaks due to satellites and second-step Auger from the continuous background caused by the shake-off decay.

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