Shake-off of loosely bound electrons in Auger decays of Kr 2p core hole states

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(Rceived 29 October 2004; published 27 October 2005)

Multicharged Kr ions have been measured using monochromatized undulator radiation combined with a coincidence technique. It has been found that a charge-state distribution of Kr ions being coincident with satellite peaks of Kr 2p3/2 photoelectron is slightly different from that for the main line. Resonant Auger peaks for 2p−1nl→1G4 nl transitions generated essentially Kr2+ only, which differs from the charge-state distribution for the normal Auger peak. These findings suggest that loosely bound electrons in high Rydberg orbitals are easily shaken-off in electron emission processes.

DOI: 10.1103/PhysRevA.72.044702 PACS number(s): 32.80.Fb, 32.80.Hd

I. INTRODUCTION

When a vacancy is created in the core orbital of an atom, it is usually filled by an Auger process in the soft x-ray region, which yields a highly charged ion [1]. Mechanisms on the formation of multicharged ions have been studied using a coincidence technique, which detects a multicharged ion in coincidence with an energy selected electron [2–7]. The decay processes were elucidated for Ar K shell, Kr M shell, Xe M shell, and other vacancies. Although decay pathways from inner shells shallower than about 1 keV were studied to some extent, limited investigations were performed for deeper orbitals. The 2p orbital of Kr is located at deeper than 1.6 keV and then measurements on multiple photoionization and electron spectroscopy have been performed in only a few studies [1,5,8,9].

Recently resonant Auger electrons and photoelectrons with satellite structures have been observed by several research groups [10–12], which has given information on ion states. These states, i.e., resonant Auger final states or photoelectron satellites, seem to have characteristics different from ion states mainly populated with conventional excitation techniques. The former states include loosely bound electrons, and these electrons are presumed to be shaken-off in subsequent Auger processes. However, studies from experimental stand points were limited for pursuing the fate of loosely bound electrons in cascade electron emission processes. It is interesting to clarify behavior of these electrons using a coincidence technique. Recent studies on the decay of the Kr 1s hole provided a clue for a shake-off probability [13], in which a sticking probability for the excited electron in the counter-part process was defined in the multiple ionization process from the 2p−1 nl states.

In the present study highly charged ions have been measured in coincidence with energy-selected electrons, which are emitted from Kr in irradiation of monochromatic soft x rays in the L-shell region. The charge state distributions are compared between a core-hole state with a loosely bound electron and that without the electron.

II. EXPERIMENT

Measurements were carried out on the soft x-ray photochemistry beam line (BL27SU) at the SPring-8 facility [14]. The photon beam was dispersed by a soft x-ray monochromator with varied-line-spacing plane gratings and introduced to the main chamber equipped with a coincidence measurement instrument [6,7]. The photon energy resolution during the measurements was set at about 2000. Photon energy was calibrated for the peak of the excitation into the 5s orbital from the 2p3/2 orbital, 1673.8 eV [12]. The monochromatized photon beam crossed the sample gas beam ejected through a 1/16-in needle at a 90° angle. The measurement apparatus is composed of a double-field type time-of-flight (TOF) mass spectrometer and a cylindrical mirror electron energy analyzer (CMA ESA-150-D Staib Instrumente). The detail of the measurement setup was described previously [6,7]. The energy width of the CMA was usually set at about 5.5 eV. A static electric field (4 V/mm) was applied to the ionization region during the coincidence measurements. This static field has not made effect on peak shapes of the electron spectra although an energy shift was observed slightly; 10 eV or so. Typical signal rates were 9000 counts/s for ions and 200 counts/s for 2p3/2 photoelectrons. Real coincidence signals depended significantly on the selected energy of electrons, ranging about 1 counts/s to about 0.05 counts/s. The sample gas pressure in the chamber was kept at 5 × 10−4 Pa during the measurements. The Kr gases with a stated purity 99.9% for the present study was purchased from Taiyo Toyo Sanso Co., Ltd.

III. RESULTS AND DISCUSSION

Time-of-flight (TOF) spectra of Kr ions at a photon energy of 1850 eV are shown in Fig. 1, for coincidence measurements with 2p3/2 photoelectrons and 2p3/2 satellite photoelectrons. The electron emission spectrum was observed at this photon energy prior to the coincidence measurements. This spectrum showed some structures around 153 eV, being about 20 eV lower than the main line of the 2p3/2 photoelec-
The present results on the 2\textsubscript{p} satellite together with results obtained using other coincidence branching ratios derived from peak areas are listed in Table I, with a similar intensity came from the Kr 6+ ion. These spectra of shallower orbitals of Kr, essentially close to those previously reported using the K α fluorescence. The 4\textsubscript{p} electrons at most cases increase their principal quantum number of a shaken-up electron can not be specified owing to low resolution of the electron energy analyzer for compensating low signal rates.

The highest intensity ratio in the coincidence with the 2\textsubscript{p3/2} photoelectron was yielded by the Kr 5+ ion and a peak at the instant of photoionization of a 2\textsubscript{p3/2} electron. This structure comes from shake-up effects of valence electrons at the instant of photoionization of a 2\textsubscript{p3/2} electron. The 4\textsubscript{p} electrons at most cases increase their principal quantum number, e.g., 5\textsubscript{p}, 6\textsubscript{p}, or other orbitals are yielded. Similar structures were reported previously for photoelectron spectra of shallower orbitals of Kr [7,10]. In the present measurement, the quantum number of a shaken-up electron can not be specified owing to low resolution of the electron energy analyzer for compensating low signal rates.

The highest intensity ratio in the coincidence with the 2\textsubscript{p3/2} photoelectron was yielded by the Kr 5+ ion and a peak with a similar intensity came from the Kr 6+ ion. These branching ratios derived from peak areas are listed in Table I, together with results obtained using other coincidence modes. The present results on the 2\textsubscript{p3/2} photoelectron are essentially close to those previously reported using the K α fluorescence coincidence technique and using characteristic x rays [1,13], although the previous data exhibited slightly higher yields for Kr\textsuperscript{4+} and lower for Kr\textsuperscript{6+} than the present ones.

The results for the coincidence mode of the 2\textsubscript{p3/2} satellites are slightly different from those for the main line. The ion with quadruple charges is formed at a lower yield, about a third, than that for the main line. The ions in higher charge states are generated at slightly higher yields. This finding suggests that about two thirds of high Rydberg electrons, which are shaken-up in the initial photoionization step of the 2\textsubscript{p3/2} electron, are shake-off in subsequent Auger transitions, producing a slightly higher charge state distribution. During the cascade decay, a participator Auger transition takes place at some extent. In this decay, the charge of the Kr ion increases by 1 only, e.g., 3\textsubscript{d}-4\textsubscript{p}→3\textsubscript{d}-4\textsubscript{p}. The latter state is presumed to be a main intermediate state for the cascade process from the main photoelectron emission, as shown in Eq. (2) below. In analogy of the spectator cascade decay model [13], the average sticking probability for the 2\textsubscript{p}→4\textsubscript{p} state is derived to be about 0.33. This value is almost the same with that estimated by Armen and co-workers, 0.34, although their value corresponds to that for the 2\textsubscript{p} state. On the other hand, average charges estimated from Table I are 5.5 for the main line and 6.0 for the satellites. This finding means that about a half of the high Rydberg electrons are shake-off in electron emission processes. A similar effect was found in our previous study, which indicated that the branching ratio of Kr\textsuperscript{2+} decreased considerably for the 3\textsubscript{d} photoelectron satellites compared to that for the main line of this photoelectron [7]. In that instance the loosely bound electron was shaken off in Auger transitions; maybe the state of 3\textsubscript{d}→4\textsubscript{p} configuration turned into those of 4\textsubscript{p} with two ejected electrons.

Let us consider the energy diagram of multi-charged Kr ion for clarification of decay pathways of the core-hole Kr ion [15]. Figure 2 depicts these energy levels in terms of one-particle approximation. The most intense Auger transition generates the \(^1\text{G}_4\) state with 3\textsubscript{d}\textsuperscript{2} configuration [8,9], which turns into Kr\textsuperscript{4+} primarily, as shown below (see Fig. 3). In the satellites coincidence mode, Auger transition probably generates some states with 3\textsubscript{d}→4\textsubscript{p}\textsubscript{nl} configuration, which exist higher than the 3\textsubscript{d}\textsuperscript{2} configuration by about 20 eV. These states are presumed to turn into 3\textsubscript{d}→4\textsubscript{p}\textsuperscript{nl} configuration through Auger shake-off transitions, and then reach 4\textsubscript{p}\textsuperscript{5} configuration, Kr\textsuperscript{5+}. Another possibility is as follows.

![Figure 1: Time-of-flight spectra of Kr ions being coincident with photoelectrons. (a) 2\textsubscript{p3/2} photoelectron. (b) 2\textsubscript{p3/2} photoelectron satellites.](image)

**Table I.** Branching ratios of highly charged Kr ions detected with the coincidence technique (in units of %).

<table>
<thead>
<tr>
<th>Selected electron</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>2\textsubscript{p3/2}</td>
<td>18±2</td>
<td>35±3</td>
<td>34±3</td>
<td>12±2</td>
<td>&lt;2</td>
<td></td>
</tr>
<tr>
<td>Satellites of 2\textsubscript{p3/2}</td>
<td>6±1</td>
<td>36±3</td>
<td>39±3</td>
<td>16±2</td>
<td>&lt;4</td>
<td></td>
</tr>
<tr>
<td>Auger (^1\text{G}_4)</td>
<td>&lt;2</td>
<td>72±4</td>
<td>27±2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resonant auger (^1\text{G}_4) \textsubscript{5s}</td>
<td>7±2</td>
<td>89±4</td>
<td>&lt;5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resonant auger (^1\text{G}_4) \textsubscript{4d}</td>
<td>6±2</td>
<td>90±4</td>
<td>&lt;5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K α fluorescence\textsuperscript{a}</td>
<td>2.3</td>
<td>31.0</td>
<td>33.1</td>
<td>25.0</td>
<td>6.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Noncoincidence\textsuperscript{b}</td>
<td>3</td>
<td>29</td>
<td>37</td>
<td>21</td>
<td>8</td>
<td>1</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Armen et al. [13].
\textsuperscript{b}Carlson et al. [1].
first Auger decay generates a triply charged ion with
$3d^{-2}4p^{-1}$ configuration through a two electron emission transition. This ion turns presumably into a quadruple-charge ion
with $3d^{-1}4p^{-3}$ and finally becomes a highly charged ion of
$5^+, 4p^{-5}$ configuration:

$$2p_{3/2}^{-1}4p^{-1}nl \rightarrow 3d^{-2}4p^{-1} + 2e \leftarrow 3d^{-1}4p^{-3} + 3e \leftarrow 4p^{-5} + 4e$$ (1)

When the Rydberg electron remains in the Kr ion with quadru-
ple charges, e.g., a configuration of $4p^{-5}nl$, this state can-
not turn into Kr$^{5+}$ energetically. The energy levels of $4p^{-5}nl$
configuration are considerably lower than that of $4p^{-2}$ con-
figuration in Kr$^{4+}$, because the binding energy of the Rydberg
electron increases with the number of the charge in the ion
core (see Fig. 2 and [12]).

Resonant Auger electron spectra have been measured at
photon energies slightly below the $2p_{3/2}$ ionization threshold,
1678.4 eV. At a photon energy of 1673 eV, considerable
yields were obtained at electron energy of 1465 eV for the
transition into the $^1G_4 5s$ state [11,12]. A similar resonant
Auger peak was observed at 1464 eV into the $^1G_4 4d$ state
when the photon energy increased to 1676 eV. Figure 3
shows TOF spectra of highly charged Kr ions being coinci-
dent with normal (into the $^1G_4$ state) and resonant Auger
electrons. Resonant Auger electrons from other final states
have a possibility to contribute to the measured spectra
slightly owing to a low resolution of the electron spectrom-
eter. Branching ratios of formation for these ions are listed in
Table I.

In the instance of the normal Auger transition, Kr$^{4+}$ is the
highest yield and Kr$^{5+}$ is formed considerably. The pathways
for formation of these ions are the following (see Fig. 2).

$$2p_{3/2}^{-1} \rightarrow 3d^{-2} + e \rightarrow 3d^{-1}4p^{-3} + 3e \rightarrow 4p^{-5} + 4e$$ (2)

Formation of highly charged Kr ions in other types of normal
Auger decays will be discussed elsewhere. The observed
spectra coincident with the resonant Auger decays show that
quadruple-charge ions are formed with extremely high ratios.
Resonant Auger transitions generate singly charged states
represented with $3d^{-2}nl$ configurations. These states are po-
sitioned at some eV’s below the states of $3d^{-2}$ configuration,
i.e., about 210 eV with reference to the neutral ground state
[11,12]. These states probably turn into triply charged states
with $3d^{-1}4p^{-2}$ configuration through a two electron emission
process; loosely bound electrons are shaken-off in an Auger
decay. In turn the triply charged state goes to the quadru-
ple-charge state. This decay pathway is given as follows:

$$3d^{-2}nl \rightarrow 3d^{-1}4p^{-2} + 2e \rightarrow 4p^{-4} + 3e.$$ (3)

The resonant Auger final states of $3d^{-2}$ nl can turn into
doubly charged states of $3d^{-1}4p^{-1}$ configuration through a
single electron emission transition, so-called participator Au-
ger decay. Since these states are located at about 120 eV,
lower than the quadruple-charge state, 128 eV, the states gen-
erate triply charged ions finally. As assumed from the results
in Fig. 3, this decay pathway has a considerably low prob-
ability. It is possible energetically that the resonant Auger
final states turn into triply charged states with $3d^{-1}4p^{-3}nl$
configurations around 190 eV through a two electron emis-

FIG. 3. Time-of-flight spectra of Kr ions being coincident with
Auger electrons. (a) Normal Auger electron into the $^1G_4$ state. (b)
Resonant Auger electron into the $^1G_4 5s$ state. (c) Resonant Auger
electron into the $^1G_4 4d$ state.
sion process. This process keeps the Rydberg electron although three 4p electrons are involved in the decay like that expressed in the lower line of Eq. (2). These states go finally to the states of Kr$^{5+}$ as the participator decay in most instances, while some of these possibly become in states of Kr$^{5+}$.

$$3d^{-2}nl \rightarrow 3d^{-1}4p^{-3}nl + 2e^{-} \rightarrow 4p^{-4} + 3e$$  \hspace{1cm} (4)

The probability ratio for processes for Eqs. (3) and (4) has been obtained to be about 7:3 using the data for the normal Auger decay on assumption of no effect of the Rydberg electron. When the Rydberg electron remains in the Kr ion with triple charges, e.g., a configuration of 4p$^{-4}$nl, this state turns into that with quadruple charges of 4p$^{-4}$ configuration only at a very low probability. These triple-charge states are positioned lower than the quadruple states within the one-particle approximation, and the multiplet splitting of 4p$^{-4}$ configuration is smaller than 5 eV [15].

Electrons in high Rydberg orbitals, 5s and 4d, seem to make a similar effect on the decay processes of electron emission, because the measured results are almost the same within experimental uncertainties (see Fig. 3 and Table I). The energy relation among several charge-state ions is suggested to play a more important role than the azimuthal quantum number of the electron of interest. The ions having five charges Kr$^{5+}$ are probably produced through some transitions which emit three or four electrons simultaneously, although these transitions take place with a very low probability. The average charge for the resonant Auger decay is about 4.0, but that for the normal Auger is about 4.3, estimated from data in Table I. This finding indicates that the average sticking probability, the concept proposed by Armen et al. [13], is 0.3 for the L$_{5}$M$_{45}$M$_{45}$ decay. This value is very close to that estimated by them, 0.34, although their value corresponds to the average of all Auger transitions and to the Rydberg electrons in $l=1$ states.

Resonant Auger final states are positioned lower than the hole state in the 3p outer shell, 214.4 eV for 3p$^{3}2$. The latter hole state generates Kr$^{3+}$ largely and Kr$^{4+}$ at some extent, according to the previous studies [4,7]. The present results shown in Fig. 3, which indicated different charge distributions from those results, seem to be contradictory to the energy relation depicted in Fig. 2. However, this contradiction can be solved through the following consideration. The fact that the resonant Auger final states have loosely bound electrons plays a crucial role through the shake-off effect for the electron emission process. The loosely bound electrons are often shaken off, inducing multiple electron emission decays. In conclusion, loosely bound electrons are easily shaken-off during cascade Auger decays into multicharged Kr ions from the 2p core hole states.

ACKNOWLEDGMENTS

We wish to express our sincere thanks to members of the staff of the SPring-8 facility for their help during the course of the experiment. This study was carried out with the approval of the SPring-8 Program Advisory committee (Grant No. 2004A0354-NSb-np). Y.M. and I.H.S. are grateful for partial financial support from the Budget of Atomic Energy Research in the Japanese Ministry of Education, Science, Sports and Culture.


(Received 2 November 2005; published 22 December 2005)

DOI: 10.1103/PhysRevA.72.069912 PACS number(s): 32.80.Fb, 32.80.Hd, 99.10.Cd

The words at the left end of the fifth and sixth rows in Table 1 on page 2 should read Resonant Auger (1G4 5s) and Resonant Auger (1G4 4d).

Equations (1) and (2) on page 3 should read

\[ 2p_{3/2}^{1/2} 4p^{-1}nl \quad 3d^{-2}4p^{-1}nl + e \quad 3d^{-1}4p^{-3} + 3e \quad 4p^{-5} + 4e \] (1)

\[ 2p^{-1} \quad 3d^{-2} + e \quad 3d^{-1}4p^{-2} + 2e \quad 4p^{-4} + 3e \quad 3d^{-1}4p^{-3} + 3e \quad 4p^{-5} + 4e^{'}. \] (2)