Multielectron transitions in x-ray absorption of krypton

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(Received 26 May 1992)

The photoabsorption cross section near the K edge in krypton gas has been measured using synchrotron radiation. Several features for simultaneous multielectron excitations were detected and analyzed by the use of the shakeup and shakeoff probabilities and their dependence on the photon energy. Previous observations of the $[1s3p]$, $[1s3d]$, and $[1s4p]$ transitions have been confirmed. A transition is found between $[1s3p]$ and $[1s3d]$ multiple excitations and identified as a three-electron excitation $[1s3d4p]$.

PACS number(s): 32.30.Rj, 32.80.Fb, 78.70.Dm

Photoabsorption of atoms has been generally treated as a single-electron excitation process. However, there is a small probability that the removal of a core electron in photoabsorption causes excitation of additional electrons in the same atom. Recently this multiple-electron excitation process in x-ray-absorption spectra has received special attention, and extensive studies in solids [1–6], gases [3–16], and vapors [17] have been performed by the use of synchrotron radiation. It was pointed out by Kodre and co-workers [3,4] and Frahm *et al.* [5] that since in solids and liquids the oscillations due to the x-ray absorption near-edge structure and the x-ray-absorption fine structure (XAFS) mask small signals in the energy region where multiple-electron excitation occurs, it is difficult to identify weak transitions in x-ray-absorption spectra. Therefore, it is usually considered at present that the measurements for multielectron excitation are possible only for monatomic gases or vapors.

For Kr gas, the measurements of x-ray-absorption spectra have been performed in the energy region of the XAFS [8] and multielectron excitation [10,11]. However, the interpretation of the x-ray-absorption structures near the K edge in Kr is not as detailed as that in Ar by Armen *et al.* [18]. It is worthwhile to observe precisely the x-ray-absorption spectra and to investigate the multielectron excitation cross sections in Kr as a function of photon energy using synchrotron radiation.

In this paper, we present the study of the multiple photoabsorption cross sections measured in an x-ray-absorption spectrum of Kr gas at room temperature. Multiple excitation effects are investigated over a 2-keV region from the Kr K edge, and the contributions from the effects of shakeup (additional electron excitation to higher bound states) and shakeoff (additional electron ejection to the continuum) to the photoabsorption spectrum are elucidated.

The absorption spectra for Kr were measured using the beam line BL-10B of the Photon Factory Ring in National Laboratory for High Energy Physics, KEK, Tsukuba, with 2.5-GeV positrons at a circular current of 260–360 mA for 24 h. The radiation was monochromatized with a Si(311) channel-cut crystal and the calculated energy resolution (combined intrinsic crystal resolution and vertical angular divergence of the beam) was less than 3 eV at the Kr K edge. The intensities of the x-ray beam were measured with two ionization chambers filled with Ar gas before and after the sample chamber. The Kr sample was contained at pressure of 0.87 and 1.19 atm in a sealed cell of 50-mm length having Kapton windows. The contribution of higher harmonics in the x-ray radiation is negligible due to the critical energy of the synchrotron-radiation spectrum. We also confirmed the absence of spurious features (glitches or multiple reflections), due to the monochromator, in $\ln(I/I_0)$, where I_0 is the intensity of incident photons and I is that of photons after passing through the Kr sample.

In Fig. 1, the measured photoabsorption cross sections in Kr are shown as a function of photon energy and compared with the theoretical values for the single-electron process (including photoelectric [19], coherent [20], and incoherent [21] cross sections) reported by McMaster *et al.* [22]. Except for conversion from absorption coefficients to cross sections, no other treatment for the raw data, such as the smoothing technique, is employed.

At high energies, the present results are smooth and the ratio of the measured cross section to the theoretical value of McMaster *et al.* [22] is almost constant. However, there exist several edges in the energy region less than

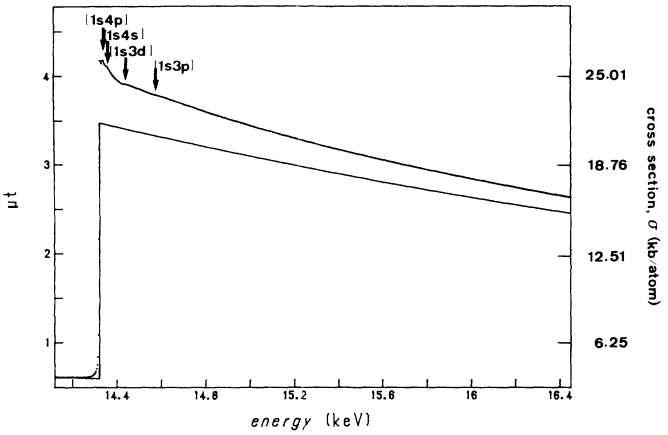

FIG. 1. Photoabsorption cross sections measured over a 2-keV region for Kr gas (dotted upper curve). The solid lower curve indicates the theoretical prediction of McMaster *et al.* (Ref. [22]).

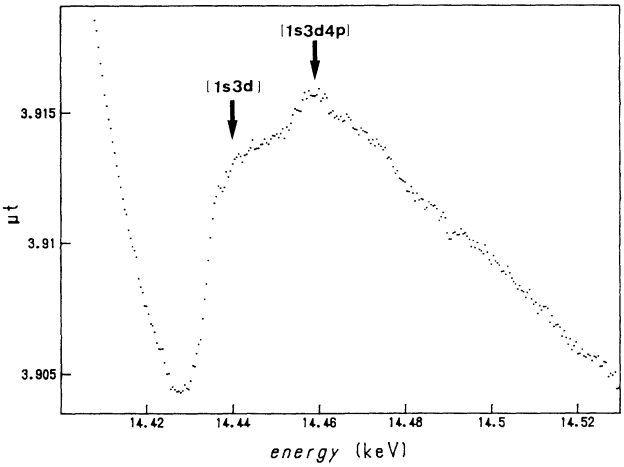

FIG. 2. Photoabsorption spectrum of Kr in the energy region for the K- plus M-shell electron excitation. The energy positions corresponding to the $[1s3d]$ and $[1s3d4p]$ edges are indicated in the figure.

250 eV above the K absorption edge. For monatomic gases such as Kr, there is no oscillatory absorption structure like the XAFS and these edges can be ascribed to the multiple-electron transition processes, i.e., the shakeup and shakeoff processes accompanying the K-shell photoionization. In Fig. 2, the existence of multielectron transitions is more clearly demonstrated in the absorption spectrum of the additional run for the limited energy region.

The assignments and energies of the various edges are summarized in Table I. Theoretical values of the energies for multiple vacancies were calculated as the difference in the total electronic energies between the ground state and the state with multiple vacancy using the Dirac-Fock (DF) method [23]. Calculations of the shakeup and shake-off probabilities were performed by the Hartree-Fock-Slater method [24]. First, the shakeup-plus-shakeoff probability was obtained in a manner similar to the method of Carlson and Nestor [25] and then the shakeup probabilities to various Rydberg states were calculated. The shakeoff probability was evaluated by subtracting the sum of shakeup probabilities from the shakeup-plus-shakeoff probability.

The $[1s3p]$, $[1s3d]$, and $[1s4p]$ edges previously observed by other workers [10,11] were confirmed in Figs. 1 and 2, where $[1snl]$ means the state with vacancies in the $1s$ and nl orbitals. The measured energies of these edges agree well with those reported by Deutsch and Hart [10], i.e., (232.6, 246.8), 113.4, and 11 eV for the $[1s3p]$, $[1s3d]$, and $[1s4p]$ edges, and also those by Bernieri and Burattini [11] (235, 113, and 16 eV, respectively). Schaphorst *et al.* have also observed quite similar results for Kr [26].

TABLE I. Electron configurations, energies, and probabilities of multielectron transitions in the K-shell photoionization of Kr. The energies are given relative to the Kr K edge and the probabilities are expressed as the ratio to the single $[1s]$ ionization.

	ΔE (keV)[a]		Probability (%)[b]	
Configuration	Calculated	Measured	P_{SU}[c]	P_{SO}[d]
$[1s3s]$	0.331		1.44[2][e]	1.97[−1]
$[1s3p_{1/2}]$	0.263	0.240	6.60[−2]	1.05
$[1s3p_{3/2}]$	0.254			
$[1s3d4s]$	0.186		7.21[−3]	2.31[−2]
$[1s3d4p]$	0.165	0.141	5.88[−2]	1.30[−1]
$[1s3d_{3/2}]$	0.125	0.115	7.07[−1]	2.79
$[1s3d_{5/2}]$	0.123			
$[1s4s]$	0.045	0.030	1.02	8.28[−1]
$[1s4p_{1/2}]$	0.027	0.015	8.31	4.67
$[1s4p_{3/2}]$	0.026			

[a]Relative to Kr K edge.
[b]Relative to the $[1s]$ probability.
[c]Shakeup probability (Ref. [24]).
[d]Shakeoff probability (Ref. [24]).
[e]1.44[−2] means 1.44×10^{-2}.

Armen *et al.* [18] measured the Auger satellite intensities of M-shell excitation accompanying the K-shell photoionization for Ar as a function of photon energy and found that the shakeup probability has a sharp threshold onset and reaches to its asymptotic value at the energy close to the threshold, while the shakeoff probability increases gradually with photon energy. Crasemann [6] and Schaphorst *et al.* [26] also pointed out the similar trend of these shake processes in the photoabsorption spectrum for monatomic gases. This fact suggests that the edges observed in x-ray-absorption spectra are due to the shakeup process only and that the shakeup-plus-shakeoff probabilities calculated by Carlson and Nestor [25] and by Mukoyama and Taniguchi [27] overestimate the experimental results.

From the experimental results in Figs. 1 and 2, we estimated the ratio of the cross section for the multiple excitation to that for the single $[1s]$ ionization. The measured ratio is $\sigma([1s3d])/\sigma([1s])\sim 4.0\times 10^{-3}$ for the $[1s3d]$ cross section and $\sigma([1s4p])/\sigma([1s])\sim 4.0\times 10^{-2}$ for the $[1s4p]$ transition. These values are in better agreement with the calculated shakeup probabilities in Table I than with the shakeup-plus-shakeoff probabilities of Carlson and Nestor [25]. The possible reasons for the discrepancy between theory and experiment are due to the error of subtracting the single-ionization cross sections and to the use of the sudden approximation, which is valid for the high-energy limit of the incident photon.

In the present work, we could not observe the one-photon–two-electron transitions involving $2s$, $2p$, and $3s$ electrons. The reason can be ascribed to too small probabilities of the shakeup process for these electrons, which are below the statistical accuracy of the present data, 0.02%. This conclusion is supported by the theoretical predictions on the shakeup probabilities in Table I and consistent with those by Schaphorst *et al.* [26].

In addition to the absorption edges reported previously, we found a transition in the x-ray-absorption spectrum in Fig. 2 between the $[1s3d]$ and $[1s3p]$ edges. The energy of this edge is determined to be 141 eV and it is assumed due to three-electron excitation involving $3d$ electrons. In the manner similar to the two-electron excitation cases, we calculated the energies of the three-electron transitions by the DF method. There are two candidates for this edge, $[1s3d4s]$ (186 eV) or $[1s3d4p]$ (165 eV). The shakeup and shakeoff probabilities for these two transitions were obtained under the assumption that the excitation processes for two electrons occur independently. The measured energy and somewhat sharp onset due to higher probability seems to favor the latter case, namely, $[1s3d4p]$.

In Table I, the calculated energies for the absorption edges are systematically higher than the measured ones. However, it should be noted that the calculated values correspond to the threshold for the multielectron ejection, i.e., the shakeoff process. As described above, the experimental results are considered to be the shakeup process. In this case, the threshold energies depend on the final-state configurations and experimentally it is very difficult to distinguish them. However, the dominant contribution to the total shakeup probability comes from the lowest possible Rydberg state, about 50% of the total shakeup probability [24]. When we approximate the threshold energy of the shakeup process as that to the state with the largest probability, we obtain the value of 18–19 eV for the $[1s4p]5p$ transition, 35 eV for the $[1s4s]5s$ transition, 114–116 eV for the $[1s3d]4d$ transition, 138–140 eV for the $[1s3d4p]4d5p$ transition, and 246–255 eV for the $[1s3p]5p$ transition. These values are in good agreement with the measured values in Table I.

We have shown that the structures in the x-ray-absorption spectrum above the Kr K edge can be explained as due to the shakeup process. The present work indicates that the understanding of the transition process involved in multiple-electron excitation is important to interpret the x-ray-absorption spectra. The observed positions of the absorption edges for multielectron transitions are in good agreement with the theoretical predictions, but the calculated shakeup probabilities overpredict the experimental values. More rigorous theoretical studies are hoped for, including correlation and relaxation effects. Experimentally, it is necessary to perform more systematic measurements on multielectron transitions in photoabsorption for various systems. Further works for other elements are in progress.

The authors would like to express their thanks to T. Åberg for valuable discussions and to B. Crasemann and A. Kodre for sending us copies of their unpublished work. Useful suggestions of M. Nomura at Photon Factory, KEK, Tsukuba, are gratefully acknowledged. One of the authors (Y.I.) expresses his appreciation to T. Shoji, Rigaku Industrial Corporation for his useful advice. This work has been performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 90-162).

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