Variation of 3s Photoionization Resonance Structures in a Serial Atomic Number Species Ar, K, and Ca

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Subvalence 3s-shell photoionization resonances of Ca were measured with monochromatized synchrotron radiation and photoion time-of-flight spectroscopy method. Charge resolved photoion yield spectra were obtained. Broad peak structures were found in the Ca\(^+\) spectrum and shallow window structures were found in the Ca\(^2+\) spectrum. We performed MCDF calculations to assign the resonance structures. The 3s-shell photoionization of Ar and K were also measured for comparison. A systematic increase was observed in Fano–Beutler parameter and in the resonance width along with the increase of atomic number from Z = 18(Ar) to 20(Ca). We discuss also the spectral structures that could be of the 3p double-shake-up satellites, which are observed in the 3s photoionization region.

KEYWORDS: atomic photoionization, alkali-earth metal, window resonance, synchrotron radiation
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1. Introduction

Inner shell photoionization resonances of rare gases or alkaline atoms have been studied extensively by many authors,\(^1\)\(^3\)\(^5\) since the transient core excited states provide us with a good probe for electron correlation effects in atoms or ions. The sub-valence s-shell photoionization of moderate or heavier atomic species is of particular interest for the distinct window type appearance of the resonance profiles. Many authors have concentrated on this aspect, and tried to explain the spectral windows in terms of the interference between the sub-valence hole state and the background continuum.\(^3\)\(^–\)\(^11\) Recently, in the 3s \(\rightarrow\) np excitations of Ar iso-electronic sequence, a dramatic change of the resonance shape along with the change of atomic number has been reported.\(^12\)\(^–\)\(^15\)

In a previous paper, we reported the window resonances of heavier alkaline atoms K,\(^16\) Rb, and Cs.\(^17\) The window resonance of these species were found to be distinctively broader compared with their neighboring rare gas atoms. Also the window shapes were found to exhibit significant differences from those in the neighboring rare gas atoms. In view of these facts, it is worthy to extend our investigation along with the serial increase of the atomic number, and try to find the systematics of window profile variations. In the present paper, we measure the charge resolved photoion yield spectra of 3s \(\rightarrow\) np excitations in neutral atomic calcium, Ca. We discuss the atomic number dependence of the window type resonance profile by comparing the spectra of Ar, K, and Ca. To enable the comparison free from the details of experimental conditions, we adopted the data of K from ref. 16 and obtained the data of Ar by performing a measurement under the same condition as of K and Ca. Although all the 3s \(\rightarrow\) np spectra give the window type resonance shape in Ar, K, and Ca, Fano–Beutler profile index \(q\) varies almost linearly against the increase of atomic number. We found more or less similar tendency also in the resonance widths. In the rest of the paper, we give a brief description of the experimental apparatus and procedure in §2, and we give results and discussion in §3. Section 4 is devoted to the summarizing remarks.

2. Experiment

We measured the spectra of photoions created by photoabsorption of gaseous atomic calcium. The photoions were charge resolved to measure the Ca\(^+\) and Ca\(^2+\) ions separately. We used the monochromatized synchrotron radiation and time-of-flight (TOF) mass spectrometer at BL-3B, Photon Factory, KEK, Japan. The TOF mass spectrometer was mounted perpendicular to both the atomic and photoion beams. The charge-state resolved spectra were measured by gated collection of the photoion TOF counts.

The apparatus is basically the same as that of our previous work,\(^1\)\(^7\) and, therefore, its detailed description will not be repeated here. The details of the monochromator at BL-3B are described in refs. 20 and 21, and the details of the TOF mass spectrometer system are described in ref. 22.

The experiment was carried out under the following conditions. The photon energy was scanned from 45 eV to 55 eV with the step size of 10 meV in the data acquisition. The photon energy was calibrated by measuring the well-known rare gas spectra.\(^6\)\(^–\)\(^9\) The target Ca-metal vapor oven was operated typically at 477°C. The Ca vapor pressure at this temperature was of the order of 10\(^{-5}\) Torr. The background gas pressure is typically the order of 10\(^{-7}\) Torr. The photoion counts are normalized to the incident photon flux of the synchrotron radiation that is monitored with the drain current from a post-focusing mirror.

To enable the comparison of serial atomic number targets free from the difference of experimental conditions, we
measured, in the present paper, the total photoion yield of Ar using the same experimental setup except the metal oven and accompanying. For the spectra of K photoionization, we refer to the result given in a previous work\textsuperscript{16} that was performed under almost the same condition.

3. Results and Discussion

Figures 1(a), 1(b), and 1(c) show the photoion yield spectra of the $3s \rightarrow np$ resonance excitation regions for Ar, K, and Ca, respectively, together with the results of theoretical energy level calculations, which will be discussed later on in detail. The spectra are plotted against the incident photon energies. Although the yields of the photoion are given in arbitrary units, the ratios of the singly and doubly charged ions in the K and Ca spectra are significant. As found in the figures, doubly charged ions are predominant in Ca photoionization, whereas singly charged ion yield is greater in the K photoionization. In all figures, we recognize the $3s \rightarrow np$ window-type resonance profiles clearly, though the higher Rydberg states are rather obscure in K and Ca. The group of the energetically lowest dip structures may be attributed to the $3s \rightarrow 4p$ sub-valence excitations, and we can point out that the $3s \rightarrow 4p$ window shape varies gradually along with the increase of the atomic number. We will be returning to this point later on. In general, we obtain the Fano–Beulter type asymmetric resonance profiles when a discrete state excitation overlaps energetically with one or several direct ionization continua. The asymmetry of the resonance shape is a good probe of the interference of a discrete state with the relevant continua. To investigate the feature of the $3s \rightarrow np$ resonance in Ar, K, and Ca, we performed Fano–Beulter profile analysis using the following profile formula.\textsuperscript{18} That is

$$
\sigma(E) = \sigma_T \left[ \frac{\rho'}{\epsilon^2 + 1} + \frac{W_{BP}}{\Gamma} - 1 \right] + 1,
$$

where the notations are defined as in the followings. They are

- $\sigma(E)$: the photoionization cross section as a function of the incident photon energy, $E$.
- $\sigma_T$: the background photoionization cross section,
- $q$: the Fano–Beulter profile parameter,
- $\Gamma$: the resonance width,
- $W_{BP}$: the monochromator bandpass width, and further on,

$$
\epsilon' = \epsilon \left( 1 + W_{BP}/\Gamma \right)^{-1},
$$

with

$$
\epsilon = (E - E_\nu) / \frac{1}{2} \Gamma,
$$

where $E_\nu$ is the resonance point energy,

$$
\rho' = \rho \left( 1 + W_{BP}/\Gamma \right)^{-1},
$$

where $\rho$ is the correlation coefficient. The experimental spectra has been fitted to the profile formula (1) by adjusting the profile index $q$, which is called the Fano or Fano–Beulter parameter, and the resonance width $\Gamma$. In the fitting procedure, we subtracted the background continuum assuming that it is linear within and in the neighborhood of the resonance; we assumed that the ionization which is irrelevant to the discrete-continuum interference vary only moderately. Table I gives the results of the fitting. In the case of Ar, we see that the values obtained are in good agreement with the recent data by Sorensen et al.\textsuperscript{8} A distinctive feature of the profile parameters that we should note here is the linear dependence of the profile index $q$ on atomic number of the target species. In Fig. 3(a), we plotted the $q$-values of $3s \rightarrow 4p$ excitations against the target atomic number $Z$. And furthermore, we give a plot of $\Gamma$ versus $Z$ in Fig. 3(b).

To assign the energy levels and to analyze the photoion yield spectral structures, we have performed a series of atomic structure calculations using one of the Multi-configuration Dirac–Fock (MCDF) codes called General purpose Relativistic Atomic Structure Program 92 (GRASP92).\textsuperscript{19} To
As for the K atoms, the details of the calculation have been more or less the same also for the cases of Ca and Ar. We interpret the reversion of the states in the Table I. Fitting results utilizing eq. (296 J. Phys. Soc. Jpn., Vol. 72, No. 2, February, 2003 M. Koide et al.)

Table I. Fitting results utilizing eq. (1) in the present work. Errors are estimated statistically.

<table>
<thead>
<tr>
<th>Main config.</th>
<th>$E_r$</th>
<th>$\Gamma$</th>
<th>$q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>$3s^3 3p^6 4p$</td>
<td>26.0(1)</td>
<td>0.074(3)</td>
</tr>
<tr>
<td></td>
<td>$3s^3 3p^6 5p$</td>
<td>28.0(1)</td>
<td>0.036(3)</td>
</tr>
<tr>
<td></td>
<td>$3s^3 3p^6 6p$</td>
<td>28.5(1)</td>
<td>0.023(5)</td>
</tr>
<tr>
<td></td>
<td>$3s^3 3p^6 7p$</td>
<td>28.7(1)</td>
<td>0.019(1)</td>
</tr>
<tr>
<td></td>
<td>$3s^3 3p^6 8p$</td>
<td>28.9(1)</td>
<td>0.020(1)</td>
</tr>
<tr>
<td>K</td>
<td>$3s^3 3p^4 4s 4p$</td>
<td>36.7(1)</td>
<td>0.205(1)</td>
</tr>
<tr>
<td></td>
<td>$3s^3 3p^4 4s 4p^{10}$</td>
<td>37.4(1)</td>
<td>0.15(1)</td>
</tr>
<tr>
<td></td>
<td>$3s^3 3p^4 4s 4p^2$</td>
<td>38.9(4)</td>
<td>0.16(1)</td>
</tr>
<tr>
<td></td>
<td>$3s^3 3p^4 4s 4p^6$</td>
<td>39.7(1)</td>
<td>0.09(1)</td>
</tr>
<tr>
<td></td>
<td>$3s^3 3p^4 4s 4p^7$</td>
<td>39.9(4)</td>
<td>0.07(1)</td>
</tr>
<tr>
<td></td>
<td>$3s^3 3p^4 4s 4p^8$</td>
<td>40.0(6)</td>
<td>0.069(6)</td>
</tr>
<tr>
<td>Ca</td>
<td>$3s^3 3p^4 4s 4p^{10}$</td>
<td>48.4(1)</td>
<td>0.28(4)</td>
</tr>
<tr>
<td></td>
<td>$3s^3 3p^4 4s 4p^{10}$</td>
<td>48.4(1)</td>
<td>0.221(6)</td>
</tr>
</tbody>
</table>

a) First state of higher series

b) Ca$^{2+}$

interpret the reversion of the states in the LS scheme of representations, we used also one of the former version GRASP2. Calculated energy positions are given in Figs. 1(a), 1(b), and 1(c) by tics above the experimental spectra. As for the K atoms, the details of the calculation have been reported previously. The procedure of the calculation is more or less the same also for the cases of Ca and Ar. We note here the crucial points. To calculate the 3s-hole states of Ar, K, and Ca, the inclusion of the mixing between 3s3d and 3p2 configurations is necessary, i.e., for example, in the Ca 3s → 4p excited state, the configurations $3s^3 3p^6 4s^2 4p^1$ and $3s^2 3p^3 3d^1 3s^3 4p^4$ mixes heavily to lower the level energy by a couple of electron volt from the results of minimal orbital set calculations. And further, although exclusively in the Ca atoms, the mixing of 4s2 and 4p2 configurations is also more necessary. We included the configurations $3s^3 3p^6 4p^2 n^1 p^1$ in the calculations of Ca 3s-hole states.

Now, we would investigate the characteristics of the photoion spectra of respective species Ar, K, and Ca. Figure 1(a) shows the photoion spectra of Ar. Because the Ar 3s → np window resonances appear far below the double ionization limit 43.38 eV,27 we measured the total ions instead of the charge resolved ones. We can see in the figure the series of 3s → np windows clearly. By a spectral analysis using eq. (1), we obtained the resonance widths and profile indices. They are given in Table I. We find the values are quite consistent to the existing data. The resonance width of the lowest energy state $3s^3 3p^6 4p^1$ is 74 meV, which is distinctively narrow compared with the corresponding widths in K and Ca. In Fig. 1(a), we also illustrate the presently calculated level energies. Considering the fact that the theoretical values are absolute, we may say that the agreement of the calculation with the experiment is satisfactory.

Figure 1(b) shows the photoion spectra of K. The dotted line is of the singly charged ion K$^+$, whereas the solid line is of the doubly charged ion K$^{2+}$. The measure of the ion count rate is illustrated on the left and right vertical axes for respective ions. Because the K-spectra has been discussed in detail in a previous paper, we note here only the points that are indispensable for the discussion in the present paper. In Table I, we give the resonance widths and resonance profile indices for observed levels. The lowest energy entry is that of the $3s^3 3p^6 4s^4 4p^1$ resonance, of which width 0.205 eV is remarkably large compared to the one in Ar. And, further on, the profile index is positive, whereas the corresponding index in Ar is negative. According to our tentative estimate, the state $3s^3 3p^6 4s^4 4p^1$ decays mainly to $3s^3 3p^3 4s^3$ ionic state, which would be stabilized by radiation. This is a good reason why we have a predominant window in the singly charged ion spectra. The weaker decay takes place in $3s^3 3p^4 4s^3 4p^4$ ionic state, which would stabilize by electron emission providing us with doubly charged ions K$^{2+}$. The slight dip at 36.7 eV in the K$^{2+}$ spectra may be attributed to this decay channel.

Figure 1(c) shows the photoion spectra of Ca. The dotted line is the singly charged ion Ca$^+$ spectrum, whereas the solid line is of the doubly charged ion Ca$^{2+}$ spectrum. The measure of the ion count rate is illustrated on the left and right vertical axes for respective ions. A remarkable feature of the spectra is that the doubly charged ions dominate for the whole energy range investigated. In the present photon energy region, the 3p direct ionization is much intense compared with the 4s direct ionization.24 The 3p direct ionization of Ca provides us with a singly charged state $3s^3 3p^6 4s^2$, which undergoes Auger decay and ends up with a doubly charged Ca ions. On the other hand, the 4s direct ionization mainly gives us the ground state of singly charged Ca ions Ca$^+$ $3s^2 3p^4 4s^1$. At around the photon energy 48.4 eV, we observe a window like structure in Ca$^{2+}$ spectra and a peak like structure in Ca$^+$ spectra, respectively. We have made an MCDF calculation for Ca 3s → 4p resonance, and obtained the values 48.4 and 48.6 eV for excitation energies. Therefore, we may assign the spectral structures at 48.4 eV are of the Ca 3s3p4s4p$^1$ state. It may be of interest that the same state gives different resonance shapes in singly and doubly charged ion channels. Similar features are also observed23 in the 37–40 eV region of Ca photoion spectra. By a spectral analysis using eq. (1), we obtained the resonance widths and profile indices. They are given in Table I. The profile index q of the Ca$^{2+}$ spectra is +0.76. In contrast to the corresponding resonance in Ar, the sign of q is positive and the magnitude is larger than the one in K by 0.53, which is almost the same as the difference of q's between K and Ar 0.51. We illustrate this situation in Fig. 3. The value of the profile index q increases almost linearly along with the increase of atomic number Z for the series Ar, K, and Ca. This suggests a systematic shift in the phase of the interference partner $3s^2 3p^4 4s^4 + \text{free electron continuum}$ with the change of Z and with w = 0, 1, and 2 for Ar, K, and Ca, respectively. In contrast to the Ca$^{2+}$ resonance, we obtained in Ca$^+$ spectra a resonance peak with q = −2.0. In this resonance, the interference partner is the Ca 4s direct ionization continuum, and the 4s ionization energy is 6.113 eV,27 which is far below the present resonance energy. The intensity of the continuum background is expected to be small enough to let the decay fraction of $3s^3 3p^6 4s^4 4p^1$ state to form a spectral peak, even though the decay from $3s^3 3p^6 4s^4 4p^1$ to $3s^2 3p^6 4s^4$ [channel (1) of
Fig. 2. Diagram of decay channels from intermediate excitation state $3s^3p^64s^24p^1$ to the ground ionic states. The channel (1) is decay to the singly charged ion final state and the channel (2) is decay to the doubly charged ion final state.

Fig. 2] is weak compared with the major Coster–Kronig decay from $3s^3p^64s^24p^1$ to $3s^3p^64s^2$ [channel (2) of Fig. 2]. For the resonance energy $E_r$ of $3s^3p^64s^24p^1$ state, we obtained 48.4 eV by spectral analysis, which is in good agreement with the present MCDF calculation 48.4 and 48.6 eV. Although the calculation has predicted the Rydberg state energy levels, which are $3s^3p^64s^25p^1$ at 51.7 eV, and $3s^3p^64s^26p^1$ at 52.4 eV, we found no clear correspondence in the experimental spectra. We suspect that a broad structure around 48 eV in $Ca^+$ spectra is actually a superposition of two peaks. One is the $3s^3p^64s^24p^1$ state at 48.4 eV, which was introduced already in the preceding paragraph, and another is a diffuse hump around 47.7 eV, which may be interpreted as one of the double shake up satellite accompanied to the $3p$-photoexcitations. We also observe in $Ca^+$ spectra similar hump structures at 49.2 eV and 49.4 eV, which we would also anticipate to be of the structures accompanied to the $3p$-photoexcitation. To verify that those structures are of such the three electron excitations, we tried to perform a theoretical calculation on a present MCDF basis. However, due to the serious correlations among the three excited orbitals, we could not obtain a satisfactory result that could bear the present discussion in accuracy. According to the recent calculation by Hibbert and Hansen, the energies of $Ca^{++} 3p^54p^2$ and $Ca^{++} 3p^55d4s$ are ranging from 41.8 to 46.3 eV. And further on, Sugar and Corliss have suggested that the $Ca^{++} 3p^54l (l = s, p, d)$ energy levels are falling in the range between 48 and 59 eV. The spectral structures we are concerned with are therefore sitting energetically in the range between $Ca^{++} 3p^5d4s$ and $Ca^{++} 3p^54l (l = s, p, d)$ states. We would suggest that the structures are of the $3p^54d15p^2$ triply excited states. Because the $3p \rightarrow 3d$ excitations are known to be very strong, we may expect a considerable amount also for $3p \rightarrow nd (n \geq 4)$ excitations. The processes of the $3p^54d15p^2$ double shake up satellite may be thus justified.

Now, finally, we consider the systematics of the photoion spectra through the species $Ar$, $K$, and $Ca$. We already noted above that the profile index $q$ of $3s \rightarrow 4p$ resonance varies almost linearly with the change of atom in number $Z$ [see Fig. 3(a)]. As noted before, the profile shape is determined by the interference of $3s^3p^64s^w4p^1$ discrete configuration with $3s^3p^64s^w$ free electron continuum with $w = 0, 1, 2$ for $Ar$, $K$, and $Ca$, respectively. The $3s \rightarrow 4p$ resonance energies $E_r$ are 26.6 eV for $Ar$, 36.7 eV for $K$, and 48.4 eV for $Ca$, respectively, whereas the lowest thresholds of $3p$ direct ionization energies are 15.760 eV for $Ar$, 24.979 eV for $K$, and 34.313 eV for $Ca$, respectively. The photoelectron energies at the resonance positions are, therefore, 10.8, 11.7, and 14.1 eV, respectively. The change of the photoelectron energy is quite moderate compared to that of photo-excitation energies. The transition dipole matrix element to the discrete state would vary considerably with $Z$, whereas the one to the direct continuum would remain rather constant. This may be the cause of the presently observed $Z$-dependence of the profile indices. We illustrate in Fig. 3(b) also the $Z$-dependence of the resonance width $\Gamma$. We find that $\Gamma$ of $K$ and $Ca$ are significantly larger than the ones of $Ar$. As discussed in ref. 16, the dominant decay channel of $3s \rightarrow 4p$ resonance level is $3s \rightarrow 3p$

Fig. 3. (a) shows the $q$ parameter versus the atomic number $Z$. (b) shows the $\Gamma$ versus the atomic number $Z$. The $\Gamma$ do not differ for $Z$. Statistical errors are shown by bar. Statistical errors are shown by bar.
Coster–Kronig type autoionizing transitions, i.e., $3s^3p^54s^44p^3$ states would predominantly decay into $3s^23p^34s^4$ free electron continuum with $w = 0, 1,$ and $2$ for Ar, K, and Ca, respectively. Because Kjersden et al.\cite{14} have reported also a quite large width in their $K^+$ ion $3s \rightarrow 4p$ resonance measurement, the presence of the 4s electrons in K and Ca cannot be the cause of the widening of resonance. The 4s electrons would behave as simple spectators on the decaying transitions. On the other hand, both the 3s and 3p electron orbitals become compact with the increase of $Z$, and would give stronger electron correlation resulting in larger resonance widths.

4. Summary

We studied the charge resolved photoion yield spectra of Ar, K, and Ca. We measured the photoion counts by means of the ion time-of-flight spectroscopy and of the monochromatized synchrotron radiation for photon energy ranges 26–30 eV for Ar, 34–42 eV for K, and 45–55 eV for Ca. The resonance state energies obtained are examined by a series of elaborate MCDF calculations. We analyzed the resonance profiles using eq. (1) and obtained a set of resonance widths and Fano–Beutler parameters, including those the newly observed Ca $3s \rightarrow np$ resonances. We pointed out that the mixing of $3s^3p^3d^1$ with $3s^13p^6$ in the ionic core electronic configurations is crucial to place the resonance level energies at right positions. The resonance width and the profile index $q$ increase significantly with the increase of atomic number of target atoms. Although we qualitatively discussed their behaviors, we note here that further detailed theoretical study will be needed to gain a solid understanding of the characteristics of the resonance spectra.

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