New Window Resonances in the Potassium $3s$ Photoabsorption Spectrum

Michi KOIDE Fumihiro KOIKE$^1$ Ralf WEHLITZ$^2$ *
Ming-Tie HUANG$^2$ † Tetsuo NAGATA$^3$ Jon C. LEVIN$^4$
Stephan FRITZSCHE$^5$ Brett D. DEPAOLA$^6$
Shunsuke OHTANI and Yoshiro AZUMA$^1$ ‡

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Institute for Laser Science, University of Electro-communications, Chofu, Tokyo 182-8585
$^1$Information Networking Center, Kitasato University, Sagamihara, Kanagawa 228-8555
$^2$Photon Factory, Institute for Materials Structure Science, KEK, Tsukuba, Ibaraki 305-0801
$^3$Department of Science and Technology, Meisei University, Hino, Tokyo 191-0042
$^4$Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996-1200, U.S.A.
$^5$Fachbereich Physik, Universitaet Kassel, Heinrich-Plett-Str. 40, D-34132 Kassel, Germany
$^6$Physics Department, Kansas State University, Manhattan, Kansas 66506, U.S.A.

Abstract

The photoion spectrum of atomic potassium was measured over the $3s \rightarrow np$ excitation region with the photoion time-of-flight method and monochromatized synchrotron radiation. An unusual spectrum with paired windows structure was found instead of a simple regular Rydberg series. Such subsidiary windows have not been observed in the $3s \rightarrow np$ resonances of Ar, which has a closed outer shell. Based on Dirac-Fock calculations, the dual window structure at 36.7 eV and at 37.4 eV was assigned to the $3s^213p^64s4p$ resonance. The line shape can be fitted by Fano’s formula and the Fano parameters were obtained.

1 Introduction

Autoionizing resonances of atoms, involving configuration mixing of discrete excited states with direct ionization continua, have been studied intensely since the first measurement of the double photoexcitation resonances of helium with synchrotron radiation. In particular, the subvalence s-shell photoexcitation in rare gas atoms and closely related species have been noted for the window type resonances, appearing as dips in the continuum background of the
photo-absorption spectrum. Window resonances are extreme cases of the Beutler-Fano profile with profile index $q$ close to zero. Such window type resonance can be of particular interest for resonances with very small oscillator-strengths since they may nevertheless appear conspicuously in the spectrum through strong interactions with the continua; and, furthermore, the spectral window depth are affected strongly by the phases of channel wavefunctions.

In the present work, we performed charge-state resolved photoion yield spectroscopy measurements of the potassium $3s \rightarrow np$ resonances with monochromatized synchrotron radiation and photoion time of flight (TOF) spectroscopy technique. Subsequently, multi-configuration Dirac-Fock (MCDF) calculations were performed in order to understand the structure of the spectrum. It was found that the $3s^3p^64snp$ series appeared prominently as window resonances in the direct $3p$ ionization continua.

2 Experiment and Results

The photoion yield spectra were measured at the 2.5 GeV electron storage ring of the Photon Factory, KEK in Tsukuba, Japan. The BL-3B bending magnet beamline with a 24m spherical grating monochromator (24-m SGM) was employed. A 200 l/mm laminar type grating was used for this experiment with 100 µm symmetric slit setting which resulted in 50 meV resolution. Monochromatized synchrotron radiation of 35 - 45 eV irradiated atomic potassium which were created by a resistive heating metal vapor oven and led into the collision chamber from the bottom. The background pressure in the experimental chamber was kept below $1.0 \times 10^{-7}$ Torr. The photoions were detected by a time of flight (TOF) mass spectrometer mounted perpendicular to both the atomic and photon beams, operating in a pulsed extraction mode. The charge-state resolved photoion yield spectra of $K^+$ and $K^{2+}$ were measured by gated collection of the photoion TOF data obtained in each step of the photon energy scan. The photoion counts were normalized by the photon flux of the synchrotron radiation monitored with the drain current from the post-focusing mirror. The photon energy calibration was accomplished by measuring the spectra of some rare gases.

The relevant part of the charge-state resolved photoion yield spectrum is shown in Fig.1. The singly charged $K^+$ yield spectrum appears very similar to the total absorption spectrum since the $K^{2+}$ yield is very small in the photon energy region of interest. Some window type features attributed to $K^+ 3s \rightarrow np$ excitations are found in the $K^+$ yield spectrum. However, their appearance is in contrast to the Ar $3s \rightarrow np$ spectrum, which shows a very sharp and regular Rydberg series up to high $n$. The potassium resonances are broader with a less clear Rydberg series structure, disappearing at lower $n$. This is true not only for neutral potassium atoms but also for potassium ions as observed previously. Since $K^+$ is isoelectronic to Ar, it can be inferred that the presence of a valence $4s$ electron does not play a decisive role in this difference. However, the most striking feature of the $K^+$ yield spectrum is a paired window structure, with the deepest and lowest feature at 36.7 eV and a smaller one right next to it at 37.4 eV, clearly too close to be the next member of the Rydberg series. Since neither the $K^+$ nor the Ar $3s \rightarrow 4p$ resonances exhibit any subsidiary dip next to the main window resonance, this can be interpreted as due to the presence of the $4s$ electron.

The resonances in the $K^+$ yield spectrum were fitted with a Fano profile for an isolated discrete state interacting with a single continuum convoluted with the 50 meV bandpass of the monochromator. The results are shown in Table 1. The photoion yield, $\sigma(E)$, is given by

$$\sigma(E) = \sigma_a \left( \frac{q + \epsilon}{\epsilon^2 + 1} \right)^2 + \sigma_b. \tag{1}$$

Here, $\epsilon(E)$ is the reduced energy and is given by $\epsilon(E) = (E - E_r)/\Gamma$, where $E$ is the incident
Figure 1: Partial photoion yields of $K^+$ (dots) and $K^{2+}$ (solid line). The scale for the $K^+$ yield is shown on the left-hand side while the scale for the $K^{2+}$ yield is shown on the right-hand side. The theoretical $3s \to np$ resonance energies are indicated in the upper part of the figure.

 photon energy, $E_r$ is the resonance energy and $\Gamma$ is the FWHM (full width at half maximum). $\sigma_a$ is the depth of the minimum associated with the resonance, and represents the portion of the continua that interacts with the discrete state. $\sigma_b$ is the portion of the continua that does not interact with the discrete state. The profile index $q$ gives the shape of the resonance. When $q$ is smaller than 1, the resonances form a dip like structure, i.e. a window resonance.

3 Calculations and Results

A series of MCDF calculations were performed by the programs GRASP92 and RATIP. We used also an older version of GRASP code (GRASP2) for the non-relativistic symmetry indices such as the total spin $S$ and the total orbital angular momentum $L$, which are useful to refer the configuration state functions expressed in terms of non-relativistic scheme of conventions. The total electronic energies of the K ground state, two series of $3s \to np$ excited states that could be assigned as either quartet $P$ or doublet $P$ in the non-relativistic sense were calculated. And the potassium ionic states with a $3s$ or $3p$ hole were also calculated. Differences in the energy of the ground state and the excited state energies correspond to the resonance energies. Also, the oscillator strengths of $3s \to np$ excitations as well as the Auger rate of $3s \to np$ excited states were obtained. Relevant results of the calculations are shown in Table 2. We found two series of photo-excitations that are comparable with the present experiment. Although the total spin
higher along with the oscillator strengths of the lower multiplicities are not good indices in a relativistic regime, we may still assign the states in terms of the total spin multiplicities as of the leading configurations in light atoms.

We would call, in the Table 2, the lower series as quartet and the higher series as doublet, hereafter, for the sake of convenience. The calculated oscillator strengths are quite small in both calculation results; i.e., the major contributions are from the quartet for the lower series in Table 2 and from the doublet for the higher series in Table 2. And further on, this means that 7% of the configuration state component is of doublet in the lower series, and, consequently, that, in this series, the photo-excitation from the ground states is realized though this minor component.

The term purity in $LS$-coupling for these states is approximately 93% based on the our calculation results; i.e., the major contributions are from the quartet for the lower series in Table 2 and from the doublet for the higher series in Table 2. And further on, this means that 7% of the configuration state component is of doublet in the lower series, and, consequently, that, in this series, the photo-excitation from the ground states is realized though this minor component. We would call, in the Table 2, the lower series as quartet and the higher series as doublet, hereafter, for the sake of convenience. The calculated oscillator strengths are quite small in both doublet and quartet $3s \rightarrow 4p$ resonances; we obtained $2.1 \times 10^{-2}$ for $2P_{1/2}$ and $2.5 \times 10^{-5}$ for $4P_{1/2}$ (see also Table 2). Due to these very small oscillator strengths, the $4P$ and $2P$ resonances in the photoionization spectra may appear as windows with the reduction of photoabsorption over the resonance positions. However, the window depths are not of the direct concern to the values of the oscillator strengths; the depths are influenced strongly by the phases of ionization channels. Nevertheless, the larger $q$ value for the $2P$ than for the $4P$ may reflect the small yet greater oscillator strength of the doublet.

Significant $3s^23p^53d^44snp$ configuration mixing with the $3s$-hole states $3s^13p^64snp$ were found. The magnitude of mixing reaches almost 25% of the total occupation, causing the total state-energy to decrease by almost 6.47 eV. Also, a significant contribution from the $3d^5$ configurations were obtained by incorporating the $d$-orbitals up to $4d$ in the MCDF wave function expansions. The $3p$ or $4s$ ionization energies can be used as benchmarks to assess the accuracy.
of the present calculation scheme. We have calculated the total energies of \( K^+ \ 3s^23p^54s^3\cdot 1P^o \), \( K^- \ 3s^23p^6 \), and \( K^{2+} \ 3s^23p^5 \) from which the ionization threshold energies with regard to the \( K \) ground state are obtained. As seen from Table 3, the results are in good agreement with previous data and support the reliability of the present calculation.

**4 Discussion**

Based on our calculated photon energy positions, the deeper window can be assigned as due to the \( 3s^33p^54s4p \) and most of the series of windows above the lowest dual windows structure can be attributed to \( 3s^33p^54snp \) resonances. The first excitation state cause the lowest dual window. Comparing the observations with the calculations, the dual window may be attributed to the resonances \( 3s \rightarrow 4p \ 1P \) and \( 2P \). The energy difference of 0.7 eV for the neighbored windows is important for this assignment. Furthermore, the resonance width calculated by RATIP is close to the observation (See Table 1). The calculation predicted another 3s3p54s4p doublet state by 2.38 eV above the deepest window, which was invisible in the present experimental spectra. This doublet \( P \) state and another doublet \( P \) state which corresponds to the first entry of the "higher series" form a pair of doublet states with the same configuration \( 3s^33p^54s4p \). The energy difference of these doublet \( P \) states 2 eV is considered as mainly from the term splitting between \( 4s4p \) singlet and triplet energies.

The main decay channel from the \( 3s \rightarrow np \) excited states is the following:

\[
3s^33p^54snp \rightarrow 3s^23p^54s + e^-
\]

in this photon energy region according to our Auger rate calculations using RATIP. On the other hand, for the continuum contributions, the predominant channel is the 3p direct ionization:

\[
3s^23p^54s + h\nu \rightarrow 3s^23p^54s + e^-
\]

Since the final state in the predominant decay channel and the predominant direct ionization channel have the same configuration, they may interfere and mix strongly if their symmetries match. Therefore both the quartet and doublet terms in the intermediate K \( 3s^33p^54snp \) state configurations require components in the continua that satisfy the symmetry condition, in order to form autoionizing resonances. Since the final ionic states have open shells and have two possible \( j \) for a 3p electron, \( j = 1/2 \) and 3/2, the \( LS \) term of final state cannot be decided uniquely.

Two thresholds of 3s direct ionization are clearly observed in the \( K^{2+} \) yield spectrum at 40.28 eV (\( 3s^33p^54s^33S \)) and at 40.67 eV (\( 3s^33p^54s^23S \)). The energy positions are in good agreement with the calculations (See Table 2). These correspond to the series limit \( 3s \rightarrow np \), \( 3s^33p^54snp^1P \) and \( 3s^33p^54snp^2P \). The limits did not appear in the \( K^+ \) spectrum. There is no clear feature at the double ionization threshold 35.971 eV in the \( K^{2+} \) spectrum. Below the 3s direct ionization threshold, a peak-like Rydberg series was found. This series may be attributed to the doublet term of \( 3s \rightarrow np \ (n \geq 5) \) excitation. Even though direct double photoionization

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**Table 3:** Our MCDF calculated results for the ionization thresholds are shown in eV unit.

| configuration         | \( 3p^6 \) | \( 3p^24s \cdot 1P^2 \) | \( 3p^24s \cdot 1P^1 \) | \( 3p^24s \cdot 3P^0 \) | \( 3p^24s \cdot 1P^1 \) | \( 3p^24s \cdot 3P^2 \) | \( 3p^24s \cdot 3P_{3/2} \) | \( 3p^24s \cdot 3P_{1/2} \) |
|-----------------------|------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| present               | 4.18       | 24.63                   | 24.75                   | 24.89                   | 25.11                   | 35.53                   | 35.81                   |
| previous*             | 4.34       | 24.49                   | 24.58                   | 24.82                   | 24.98                   | 35.97                   | 36.24                   |

*Sugar and Corliss\(^{27,28}\) and Catalán and Rico\(^{29}\)
is energetically possible above 35.971 eV, it is very weak compared to the single ionization process in this energy region. Hence, the \(^2P\) series, with a much larger oscillator strength, appear as a peak like Rydberg series in the \(K^{2+}\) yield spectrum.

5 Summary

In summary, the \(3s \rightarrow np\) photoexcitation resonances of atomic potassium were observed between 35.5 eV and 40 eV incident photon energy through charge state resolved photoion spectroscopy. New paired windows and series of windows were observed for the first time and they were assigned as \(3s^33p^64snp\). The assignments have been made based on the results of our MCDF calculations. The valence 4s electron of K induces the term energy splitting by electron correlation, and hence, the two states could be resolved. This new dual window feature could be attributed to \(3s^33p^64s4p \, ^3P\) and \(^2P\). Since the \(^3P\) assignment would mean an \(LS\) forbidden transition, it requires further scrutiny, although the good agreement between the calculated and observed energy positions is very suggestive. More thorough investigations both theoretically and experimentally are needed for an unambiguous interpretation of this process.

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