Multielectron spectroscopy: 
Energy levels of K$^{n+}$ and Rb$^{n+}$ ions (n = 2, 3, 4)

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Abstract

A magnetic bottle time of flight spectrometer has been used to perform spectroscopy of K$^{n+}$ and Rb$^{n+}$ states with ionization degrees n of 2, 3 and 4. Energy levels are directly measured by detecting in coincidence the n electrons that are emitted as a result of single photon absorption. Experimental results are compared with the energies from the NIST atomic database [1] and ab initio multiconfiguration Dirac-Fock calculations. Previously unidentified 3p$^4$(3P)3d$^1$ 4D energy levels of K$^{2+}$ are assigned.
1. Introduction

Electron spectroscopy has become an important field for the study of the electronic structure of matter. The increasing availability of modern X-ray light sources with high tunability, high brightness and narrow photon-energy bandwidth has allowed a deep exploration of photoionization phenomena in gases, liquids and solids. The multielectron coincidence spectroscopy is a technique that aims to detect all the electrons emitted as a result of single photon absorption. It is based on a magnetic bottle time of flight spectrometer developed by Eland et al. [2] and has been combined with synchrotron radiation [3,4] to study multiple photoionization processes in atoms and molecules [5–18]. Detailed information on single core hole and, more recently, on double core hole ionization has been obtained by this technique [19–24]. In addition, precise information on ions can be obtained. An example is core-valence double photoionization of neutral atoms where a single photon absorption leads to the emission of two photoelectrons: one from a valence shell and the other one from an inner shell [10]. Such processes studied with multi-electron coincidence spectroscopy give information which is directly comparable to the direct core photoionization of the related singly charged ion, which is a challenging and difficult experiment when performed with ion-photon merged beams setups [25].

In this work we will focus on the spectroscopy of alkali atoms and in particular we will show that our experimental setup has been successfully used to perform a direct measurement of the energy levels of doubly, triply and quadruply charged potassium and rubidium ions. In a previous study [26], binding energies of Hg$^{3+}$ and Hg$^{4+}$ have been determined by multielectron coincidence technique thus providing complementary information to NIST database [1].

Potassium and rubidium are part of the alkali-metals family which is characterized by an electronic configuration composed of a rare gas core and an outer shell ns electron: K= [Ar] 4s$^1$ and Rb= [Kr] 5s$^1$ with low ionization potentials 4.3407 eV and 4.1771 eV, respectively [1]. The spectroscopy of these elements has been widely studied since the 1930s [27–32] and a large literature exists which is compiled in references [33] and [34]. The experiments consisted in exciting or ionizing the system with a sliding spark and measuring the emitted radiation (i.e. energy difference between two atomic levels) with a spectrograph. By identifying the ground state and by assigning correctly the energy lines one can deduce the energy levels of the system. On the theory side, this assignment was possible thanks to detailed semi-empirical calculations. In recent years, advances in both theory and experiment lead to improvement of the previous results. The experiment of Pettersen et al. [35] reported more than 120 new lines in K II which were identified as levels of 3p$^5$3d$^1$, 3p$^5$4f$^1$, 3p$^5$5f$^1$ and 3p$^5$6f$^1$ configurations. Recently, in a different kind of experiments using merged ion and synchrotron beams, Alna'Washi et al. [36] reported a more precise measurement of the K$^{2+}$ ionization threshold at 45.717 eV, 0.089 eV lower than the
value tabulated in the NIST database [1], which demonstrates the needs to explore critically the results of these early spectrographic investigations.

The goal of the present investigation was to measure directly the energy levels of K$^{2+}$, K$^{3+}$, K$^{4+}$, Rb$^{2+}$, Rb$^{3+}$ and Rb$^{4+}$ ions thanks to our multielectron coincidence technique. We have found that energy levels for rubidium are in good agreement with the tabulations of the NIST database, but this it is not the case for potassium; in particular for K$^{2+}$ states, we have identified an intense peak which is not reported. We have performed ab initio multiconfiguration Dirac-Fock and Hartree Fock calculations that assign this peak to the 3p$^4$ (3P) 3d$^1$ 4D$_J$ (J=1/2, 3/2, 5/2, 7/2) states. The experiment and comparison to the calculations show also that many of the K$^{2+}$ lines are identified incorrectly in the NIST database.

2. Experiment

The experiment was carried out at the PLEIADES undulator beamline [37] of the SOLEIL synchrotron facility during the single bunch operating mode that provides bunches of light every 1184 ns. A magnetic bottle time of flight spectrometer called HERMES [3] (High Energy Resolution Multi-electron Spectrometer) is used to detect in coincidence all the electrons that are emitted after absorption of a single photon. Briefly, electrons are repelled from the ionization area by the inhomogeneous field of a strong permanent magnet (0.7 T) (magnetic mirror configuration) and guided through a 2m long solenoid (1 mT) towards the detector which is a set of micro channel plates (MCP). A phosphor screen is used to visualize the image of electron impacts which is useful for optimizing the position of the permanent magnet in the ionization region. The time of flight of each electron is recorded by a time to digital converter with 275 ps discretization step. Calibration and conversion to kinetic energy is achieved by measuring photoelectrons of He at different photon energies. The relative energy resolution of the spectrometer is estimated to $\Delta E/E= 1.6\%$ for electron kinetic energies $E > 1eV$. The overall detection efficiency is deduced by comparing, at different excess energies, the number of Auger electrons of the Argon 2p hole detected with and without coincidence with the 2p photoelectron. The obtained value is 65% ± 5%, it remains constant for electrons having less than 100 eV kinetic energy and decrease slightly for higher kinetic energies. This allows the effective detection up to 4 electrons in coincidence. A mechanical chopper enables us to select only one light bunch every 12.5 $\mu$s thanks to this which we can measure the absolute electron time of flight [38], without any overlap with the contributions of the successive selected photon bunches. Potassium and rubidium vapors are produced by a homemade resistively heated oven and are effusing through a heated tube, 1 mm in diameter, 15 mm in length, that keeps the vapor beam collimated.

3. Calculations
Calculations of the ground and double ionized states of potassium atom were carried out in non-relativistic multiconfiguration Hartree-Fock (MCHF) and relativistic multiconfiguration Dirac-Fock (MCDF) schemes. The HF wave functions with relativistic corrections were computed using the COWAN code [39] and for the calculations of the relativistic wave functions of the one electron spin orbitals GRASP2K code package was used [40]. The optimization of the radial wave functions was performed in the average level (AL) scheme. The atomic state functions (ASFs) for bound states were obtained by diagonalizing the Hamiltonian matrix in the basis of antisymmetric configuration state functions (CSFs). In the GRASP case this was done with RELCI component of the RATIP package [41,42]. Also the jj-coupled ASFs were changed to LSJ-coupled basis using the TOOLBOX component of the RATIP package.

In order to obtain the binding energies of the K\(^{2+}\) states, first the energies and eigenvectors of neutral potassium atom [Ar] 4s\(^1\) were calculated. Two basis sets, first including 3s\(^1\)3p\(^6\), 3s\(^2\)3p\(^4\) (3d, 4s, 4d, 5s)\(^1\) even parity configurations and second including 3s\(^2\)3p\(^5\) and 3s\(^2\)3p\(^4\)4p\(^1\) odd parity configurations were used in the calculations for the K\(^{2+}\) states. The calculated energy levels of K\(^{2+}\) states together with the experiment and energies from NIST are presented in Fig. 8. The calculated values are aligned to match the experimental binding energy of the K\(^{2+}\) 3s\(^1\)3p\(^6\) 2S state by adding 1.94 eV and 1.04 eV to the calculated MCDF and MCHF binding energy values, respectively.

4. Results and discussions
4.1 Overview of K\(^n+\) and Rb\(^n+\) levels

In this experiment we investigate single photon multiple ionization processes:

\[ h\nu + X \rightarrow X^n + + n \ \text{e}^- , \]  

(1)

in which \( h\nu \) is the photon energy, \( X \) corresponds to K or Rb atom and \( n \) is the number of emitted electrons (\( n = 2, 3 \) or 4). Our experimental data consist in a set of listed photoionization events. For each event, all the electrons detected are recorded by their time of flight. One can thus study independently each \( X^n + \) ion by selecting events where \( n \) electrons are detected in coincidence. Binding energy \( E_{BE} \) of the \( X^n + \) state created according to (1) is calculated as follows:

\[ E_{BE} = h\nu - \sum_{i=1}^{i=n} E_i , \]  

(2)

where \( E_i \) is the kinetic energy of the electron number \( i \). Figures 1-6 represent experimental spectra for K\(^{2+}\), Rb\(^{2+}\), K\(^3+\), Rb\(^3+\), K\(^4+\) and Rb\(^4+\), respectively, and show the histograms of the kinetic energy sum of the \( n \) electrons in coincidence recorded at several photon energies and plotted as a function of the corresponding ion’s binding energy. The experimental results are compared with the binding energies tabulated in NIST database [1] shown as vertical bars at the bottom of the spectra.

The doubly ionized states of potassium are presented in Fig. 1. The experimental resolution is determined by the resolution of the magnetic bottle spectrometer, which is much larger than the photon energy bandwidth. As the energy
resolution of the apparatus $\Delta E$ for one electron is best for electrons of lower kinetic energy $E$ ($\Delta E/E=1.6\%$), the different groups of states are better resolved when selecting photon energies slightly in excess of their binding energies. At 44.5 eV photon energy, the $K^{2+}$ ground state doublet $3s^23p^6 \ ^2P_{3/2}$ and $\ ^2P_{1/2}$ is resolved; we observe an energy splitting of $0.26 \pm 0.02$ eV in agreement with the value of 0.26848 eV tabulated in the literature [1]. At 80 eV and 100 eV photon energy, the doublet is no longer resolved but states at higher energy are accessible. At $h\nu=80$ eV $3s^13p^6$, $3s^23p^43d^1$, $3s^23p^44s^1$, $3s^23p^44p^1$ and $3s^23p^4 \ ^3P$ 5$s^1$ states are populated. An increased background for high binding energy ($E_{BE}>70$ eV) is due to random coincidences involving electrons of low kinetic energies generated by surface processes. In the spectrum measured at $h\nu=100$ eV photon energy, also $3s^23p^4 \ ^1D$ 5$s^1$ and $3s^23p^4 \ ^3P$ 3$d^1$ states are seen. With both 80 eV and 100 eV photon energy we distinguish clearly a peak located at 56.83 $\pm$ 0.03 eV (labelled with “A” in Fig. 1) that has a comparable intensity to the $3s^13p^6$ state but which is not tabulated in NIST database. The other observed peaks, which are not assigned in NIST tables, have much less intensity and are labelled with a “*” mark.

The experimental spectra recorded using 46 eV, 70 eV and 90 eV photon energies showing doubly ionized states of rubidium are presented in Fig. 2. Firstly, a double ionization threshold has been measured with 46 eV photon energy. The spin orbit splitting of the $Rb^{2+} \ 4s^24p^5 \ ^2P$ state is 0.9132 eV [1] which is larger than the corresponding splitting in $K$. The doublet $4s^24p^5 \ ^2P$ is resolved also at the higher photon energy used here. 70 eV photon energy leads to the population of the $4s^24p^5$, $4s^24p^4d^1$, $4s^24p^4s^1$, and $4s^24p^4p^1$ states. Finally, 90 eV photon energy allows us to populate the $4s^24p^46s^1$ and $4s^24p^45d^1$ states.

Figures 3 and 4 present triple ionized states of K and Rb, respectively, obtained by selecting events where three electrons are detected. For $K^{3+}$, the $^3P$ terms of the $3s^23p^4$ configuration are not resolved in our experiment. Instead, in the $Rb^{3+}$ case the spin-orbit splitting being larger, we can resolve the $^3P_0$ term from the $^3P_{1,2}$ ones even with 140 eV photons. The weaker signal for $K^{3+}$ ions reflects the lower triple photoionization cross section of K compared to Rb at these photon energies. In fact, above 110 eV photon energy the decay of the Rb 3$d$ hole populates efficiently $Rb^{3+}$ states. Note that photon energy 113.5 eV coincides with the excitation energy of the $3d_{5/2}$ to the $5p$ [43] and $Rb^{3+}$ species can be formed via resonant triple Auger decay at this photon energy. At 140 eV photon energy, we are above the $3d$ threshold and $Rb^{3+}$ are then efficiently populated by normal double Auger processes. These considerations are confirmed by the relative abundances of $K^+$, $K^{2+}$ and $K^{3+}$ ions produced at 100 eV and 180 eV photon energy compared with relative abundances of $Rb^+$, $Rb^{2+}$ and $Rb^{3+}$ ions produced at 90 eV, 113.5 eV and 140 eV (see Table 1). Our results show clearly that triply ionized states of Rb are predominantly populated at 140 eV via the double Auger of the $3d$ hole.
<table>
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<th>Rubidium</th>
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<td>180 eV</td>
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Table 1: Relative abundances (%) of potassium and rubidium ions at several photon energies. They have been deduced from the number of detected coincidence counts, taking into account the detection efficiencies.

Figures 5 and 6 presents quadruply ionized states of K and Rb, respectively. Here, the photon energies are above inner shell ionization in both K and Rb (2p in K and 3d in Rb), and quadruply charged ions originate from complex Auger decays. Groups of states with low binding energy range correspond to the configurations $3s^23p^3$ in K$^{4+}$ and $4s^24p^3$ in Rb$^{4+}$ and the energy splitting between $4S$, $2D$, and $2P$ terms is higher in Rb$^{4+}$ than in K$^{4+}$. The next group of states are $3s^13p^4$, $3s^23p^23d^6$ and $3s^23p^24s^1$ for K and similarly $4s^14p^4$ and $4s^24p^25s^1$ for Rb.

### 4.2 Assignment of the K$^{2+}$ missing state

In Fig. 7 we compare measurements obtained for both K$^{2+}$ and Rb$^{2+}$. Energy levels have a similar structure at lower binding energy: a doublet of ns$^2np^5$ states followed by ns$^1np^6$ state and at higher energy the remaining states. This is obvious since the similar electronic structure of Rb$^{2+}$ and K$^{2+}$. The rubidium spectrum exhibits a larger spin orbit splitting than the potassium, which is clearly seen in the ns$^2np^5$ states. For Rb$^{2+}$ there are more tabulated energies in NIST tables. Primary data source [33,44] for K$^{2+}$ energy levels in NIST are based on 3 experiments that date back to the 1930s: the measurements of Bowen [27], de Bruin [45] and Ekefors [46]. On the other hand, the first experiment on Rb$^{2+}$ was in 1938 [30] but J. Reader et al. [47] and J. E. Hansen et al.[48] performed more advanced measurements in the 1970s.

An important information that can be extracted from Fig. 7 is the non-tabulated peak located at 56.83 ± 0.03 eV marked ‘A’ in the potassium spectrum. The analogue peak in the rubidium spectrum corresponds to the group of states marked ‘B’ located at 50.67 ± 0.03 eV with the configuration $4s^24p^4(3P)4d^4 4D_j$ (J=1/2, 3/2, 5/2, 7/2). This suggests that the non-tabulated peak corresponds to a $3s^23p^4(3P)3d^4 4D$ configuration also in K. A comparison can also be made with singly charged argon ion, which is isoelectronic with the K$^{2+}$ ion. Tabulated energy levels of Ar$^+$ in NIST includes the configuration $3s^23p^4(3P)3d^4 4D$. This state was not observed by conventional electron spectroscopy, even in the more recent high resolution Ar$^+$ photoelectron spectrum obtained using a He lamp [49] or synchrotron radiation [50]. The reason is that in photoionization of $^1S$ Ar atoms, one populates preferentially Ar$^+$ ions of $^2P$ and $^2S$ symmetries. The weak population of the Ar$^+$ $3s^23p^4(3P)3d^4 4D$ state by photoionization was however detected with the threshold photoelectron technique [51], because this state can be populated via autoionization with emission of a low energy electron of a doubly excited state of Ar$^{**}$ lying at 32.21 eV.
To confirm our experimental finding we perform ab initio calculations shown in Fig. 8 that are in good agreement with [52]. Red lines in Fig. 8 connect predicted binding energy value to the NIST binding energy value of the corresponding state. Blue lines connect the energy levels corresponding to $3s^23p^43d^1$ states, which are not found in the reference tables and green lines connect the states that are identified differently in the HF and MCDF calculations. In general, although some of the predicted states are missing in NIST database, reasonable agreement is found between the experiment, NIST and calculations under the 65 eV binding energy range. The ordering of the states obtained in HF scheme seems to be more consistent with the previous assignments than MCDF calculations, but the binding energy splitting are slightly better determined by the MCDF calculation. Scaling options for the HF Coulomb radial integrals in the Cowan’s code for compensating the missing electron correlation was not used, although it is empirically known to produce better agreement with experimental energy levels. Both calculations (with HF and MCDF schemes) confirm the presence of the $3s^23p^4(^3P)3d^1 4^D$ states around 57 eV binding energy.

From Fig. 8 one can see that for the binding energies above 65 eV, the differences in assignments of the tabulated energy levels from NIST and predicted energy levels from calculations are generally significantly larger, which may indicate that some of the assignments of these states are not correct. According to calculations, there also should be a number of missing $3s^23p^44d$ states around 70-75 eV binding energy, where also some structure can be observed in the experimental spectra. These observations indicate that the state assigned as $3p(^3P)3d^1 2^D$ would instead belong to the $3s^23p^44d$ (or $3s^23p^45s$) configuration.

5. Conclusion

In this paper, we investigated $K^{n+}$ and $Rb^{n+}$ ($n=2, 3, 4$) energy levels with multielectron coincidence technique. Our results show generally a very good agreement with NIST compiled data. We were able to perform the spectroscopy of each ion by detecting all the electrons that are emitted in coincidence.

In addition, we observed a previously unassigned peak located at 56.83eV binding energy in $K^{2+}$ spectrum. The comparison with previous study of $Rb^{2+}$ and $Ar^+$ energy levels together with theoretical predictions with HF and MCDF schemes, allowed us its assignment as the $K^{2+} 3s^23p^4 (^3P) 3d^0 4^D$ state.

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Figure 1: Histogram of the energy sum of two electrons detected in coincidence recorded at several photon energies. Vertical bars correspond to $K^{2+}$ energy levels compiled in NIST [1]. The peak labelled A has been assigned to the $3s^23p^4(^3P)3d^4D$ state.
Figure 2: Histogram of the energy sum of two electrons detected in coincidence recorded at several photon energies. Vertical bars corresponds to Rb$^{2+}$ energy levels compiled in NIST [1].

Figure 3: Histogram of the energy sum of three electrons detected in coincidence recorded at several photon energies. Vertical bars corresponds to K$^{3+}$ energy levels compiled in NIST [1].
Figure 4: Histogram of the energy sum of three electrons detected in coincidence recorded at several photon energies. Vertical bars correspond to Rb$^{3+}$ energy levels compiled in NIST [1].

Figure 5: Histogram of the energy sum of four electrons detected in coincidence recorded at several photon energies. Vertical bars correspond to K$^{4+}$ energy levels compiled in NIST [1].
Figure 6: Histogram of the energy sum of four electrons detected in coincidence recorded at several photon energies. Vertical bars corresponds to Rb$^{4+}$ energy levels compiled in NIST [1].
Figure 7: Histogram of the energy sum of two electrons detected in coincidence for Rb (top) and K (bottom). Vertical bars correspond to energy levels compiled in NIST [1]. The peak labelled “B” in Rb, which corresponds to the 4s\(^2\)4p\(^4\) (3p) 4d\(^4\)D state, is the analogue of the peak labelled “A” in K (not compiled in NIST). We assign the peak A to the 3s\(^2\)3p\(^4\) (3p) 3d\(^4\)D state.
Figure 8: Assignment of the K$^{2+}$ energy levels. The K$^{2+}$ spectrum is measured at photon energy of 100 eV shown in Figure 1. The predicted binding energies obtained with HF (Cowan) and MCDF (Grasp) schemes are compared with experimental binding energies from NIST [1].