



HAL
open science

Multielectron spectroscopy: energy levels of $K n +$ and $Rb n +$ ions ($n = 2, 3, 4$)

M. A Khalal, J Soronen, J Jänkälä, M Huttula, M Bizau, D. Cubaynes, S Guilbaud, K. Ito, L. Andric, J. Feng, et al.

► To cite this version:

M. A Khalal, J Soronen, J Jänkälä, M Huttula, M Bizau, et al.. Multielectron spectroscopy: energy levels of $K n +$ and $Rb n +$ ions ($n = 2, 3, 4$). *Journal of Physics B: Atomic, Molecular and Optical Physics*, 2017, 50 (22), pp.225003. 10.1088/1361-6455/aa90d6 . hal-02106816

HAL Id: hal-02106816

<https://hal.science/hal-02106816v1>

Submitted on 14 Nov 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

M. A. Khalal¹, J. Soronen², K. Jänkälä², S.-M. Huttula², M. Huttula²,
J-M Bizau^{3,4}, D. Cubaynes^{3,4}, S. Guilbaud³, K. Ito⁴,
L. Andric^{1,5}, J. Feng¹, P. Lablanquie¹, J. Palaudoux¹, and F. Penent¹

¹*Sorbonne Université, UPMC Université Paris 06, CNRS, LCP-MR (UMR 7614), 4
place Jussieu, 75252 Paris Cedex 05, France*

²*Nano and Molecular Systems research unit, University of Oulu, P.O. Box 3000,
90014 University of Oulu, Finland*

³*ISMO, CNRS UMR 8214, Université Paris-Sud, Bâtiment 350, F-91405 Orsay,
France*

⁴*Synchrotron SOLEIL, l'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-
Yvette Cedex, France*

⁵*Université Paris-Est, 5 boulevard Descartes, F-77454 Marne-la-Vallée cedex 2,
France*

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: $\text{K} = [\text{Ar}] 4s^1$ and $\text{Rb} = [\text{Kr}] 5s^1$ 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 $E > 1\text{eV}$. 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 $65\% \pm 5\%$, 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 μs 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 to 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:

$$h\nu + X \rightarrow X^{n+} + n e^-, \quad (1)$$

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:

$$E_{BE} = h\nu - \sum_{i=1}^{i=n} E_i, \quad (2)$$

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 ΔE 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 $3s^23p^5\ ^2P_{3/2}$ and $\ ^2P_{1/2}$ is resolved; we observe an energy splitting of 0.26 ± 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 $3s^23p^4\ (^3P)\ 5s^1$ 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 $3s^23p^4\ (^1D)\ 5s^1$ and $3s^23p^4\ (^3P)\ 3d^1$ states are seen. With both 80 eV and 100 eV photon energy we distinguish clearly a peak located at 56.83 ± 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 $4s^14p^6$, $4s^24p^44d^1$, $4s^24p^45s^1$, and $4s^24p^45p^1$ 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 $3d$ 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.

Degree of ionization	Potassium		Rubidium		
	$h\nu=100$ eV	180 eV	90 eV	113.5 eV	140 eV
N=1	56.1	52.4	43	4.5	9.1
N=2	41.8	38.4	52.9	61.0	23.5
N=3	2.1	9.2	4.1	34.5	67.4

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 $3s^13p^4$, $3s^23p^23d^1$ 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 $4s^24p^4(^3P)4d^1\ ^4D_J$ ($J=1/2, 3/2, 5/2, 7/2$). This suggests that the non-tabulated peak corresponds to a $3s^23p^4(^3P)3d\ ^4D$ 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 $3s^23p^4(^3P)3d^1\ ^4D$. 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 $Ar^+ 3s^23p^4(^3P)3d^1\ ^4D$ 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 $3s^23p^4(^3P)3d^1\ ^4D$ 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 $3p^4(^3P)3d^1\ ^2D$ 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 $K^{2+} 3s^23p^4 (^3P) 3d^1\ ^4D$ state.

6. Acknowledgments

The experiment was performed at SOLEIL Synchrotron (France) at the PLEIADES beam line, with the approval of the Soleil Peer Review Committee (Projects No. 20120132 and 20131019). We are grateful to X-J. Liu, C. Miron, C. Nicolas, E. Robert and PLEIADES teams for help during the measurements, and to SOLEIL staff for stable operation of the storage ring. M. A. K. acknowledges the support of the Labex Plas@Par managed by the Agence Nationale de la Recherche, as part of the

“Programme d’Investissements d’Avenir” under Reference No. ANR-11-IDEX-0004-02. EXACTUS doctoral program, Tauno Tönning foundation and Magnus Ehrnrooth foundation are acknowledged by J. S. for their support. This work has been financially supported by the Research Council for Natural Sciences and Engineering of the Academy of Finland.

References

- [1] Anon Kramida, A., Ralchenko, Yu., Reader, J. and NIST ASD Team (2015). NIST Atomic Spectra Database (version 5.3), [Online]. Available: <http://physics.nist.gov/asd> [Fri Jun 10 2016]. National Institute of Standards and Technology, Gaithersburg, MD.
- [2] Eland J H D, Vieuxmaire O, Kinugawa T, Lablanquie P, Hall R I and Penent F 2003 Complete Two-Electron Spectra in Double Photoionization: The Rare Gases Ar, Kr, and Xe *Phys. Rev. Lett.* **90** 053003
- [3] Penent F, Palaudoux J, Lablanquie P, Andric L, Feifel R and Eland J H D 2005 Multielectron Spectroscopy: The Xenon 4 d Hole Double Auger Decay *Phys. Rev. Lett.* **95** 083002
- [4] Penent F, Lablanquie P, Hall R I, Palaudoux J, Ito K, Hikosaka Y, Aoto T and Eland J H D 2005 Coincidence Auger spectroscopy *J. Electron Spectrosc. Relat. Phenom.* **144–147** 7–11
- [5] Palaudoux J, Lablanquie P, Andric L, Ito K, Shigemasa E, Eland J H D, Jonauskas V, Kučas S, Karazija R and Penent F 2010 Multielectron spectroscopy: Auger decays of the krypton 3 d hole *Phys. Rev. A* **82** 043419
- [6] Andersson E, Fritzsche S, Linusson P, Hedin L, Eland J H D, Rubensson J-E, Karlsson L and Feifel R 2010 Multielectron coincidence study of the double Auger decay of 3 d -ionized krypton *Phys. Rev. A* **82** 043418
- [7] Lablanquie P, Andric L, Palaudoux J, Becker U, Braune M, Viefhaus J, Eland J H D and Penent F 2007 Multielectron spectroscopy: Auger decays of the argon 2p hole *J. Electron Spectrosc. Relat. Phenom.* **156–158** 51–7
- [8] Penent F, Lablanquie P, Palaudoux J, Andric L, Gamblin G, Hikosaka Y, Ito K and Carniato S 2011 Unveiling Residual Molecular Binding in Triply Charged Hydrogen Bromide *Phys. Rev. Lett.* **106** 103002

- [9] Lablanquie P, Penent F, Palaudoux J, Andric L, Selles P, Carniato S, Bučar K, Žitnik M, Huttula M, Eland J H D, Shigemasa E, Soejima K, Hikosaka Y, Suzuki I H, Nakano M and Ito K 2011 Properties of Hollow Molecules Probed by Single-Photon Double Ionization *Phys. Rev. Lett.* **106** 063003
- [10] Huttula S-M, Lablanquie P, Andric L, Palaudoux J, Huttula M, Sheinerman S, Shigemasa E, Hikosaka Y, Ito K and Penent F 2013 Decay of a 2 p Inner-Shell Hole in an Ar + Ion *Phys. Rev. Lett.* **110** 113002
- [11] Lablanquie P, Penent F and Hikosaka Y 2016 Multi-electron coincidence spectroscopy: double photoionization from molecular inner-shell orbitals *J. Phys. B At. Mol. Opt. Phys.* **49** 182002
- [12] Palaudoux J, Sheinerman S, Soronen J, Huttula S-M, Huttula M, Jänkälä K, Andric L, Ito K, Lablanquie P, Penent F, Bizau J-M, Guilbaud S and Cubaynes D 2015 Valence Auger decay following 3 s photoionization in potassium *Phys. Rev. A* **92** 012510
- [13] Lablanquie P, Sheinerman S, Andric L, Palaudoux J, Hikosaka Y, Ito K and Penent F 2012 Post collision interaction probed by multi-electron coincidences: Application to the Ar 2s inner-shell photoionization *J. Electron Spectrosc. Relat. Phenom.* **185** 198–203
- [14] Eland J H D, Feifel R and Edvardsson D 2004 Single and Double Photoelectron Spectroscopy of Atomic Mercury [†] *J. Phys. Chem. A* **108** 9721–5
- [15] Linusson P, Takahashi O, Ueda K, Eland J H D and Feifel R 2011 Structure sensitivity of double inner-shell holes in sulfur-containing molecules *Phys. Rev. A* **83** 022506
- [16] Andersson J, Beerwerth R, Linusson P, Eland J H D, Zhaunerchyk V, Fritzsche S and Feifel R 2015 Triple ionization of atomic Cd involving 4 p – 1 and 4 s – 1 inner-shell holes *Phys. Rev. A* **92**
- [17] Andersson J, Beerwerth R, Roos A H, Squibb R J, Singh R, Zagorodskikh S, Talaei O, Koulentianos D, Eland J H D, Fritzsche S and Feifel R 2017 Auger decay of 4 d inner-shell holes in atomic Hg leading to triple ionization *Phys. Rev. A* **96**
- [18] Lablanquie P, Khalal M A, Andric L, Palaudoux J, Penent F, Bizau J-M, Cubaynes D, Jänkälä K, Hikosaka Y, Ito K, Bučar K and Žitnik M 2017 Multi-electron coincidence spectroscopy: Triple Auger decay of Ar 2p and 2s holes *J. Electron Spectrosc. Relat. Phenom.* ISSN 0368-2048, doi: <http://dx.doi.org/10.1016/j.elspec.2017.04.003>
- [19] Carniato S, Selles P, Andric L, Palaudoux J, Penent F, Žitnik M, Bučar K, Nakano M, Hikosaka Y, Ito K and Lablanquie P 2015 Single photon simultaneous K-shell ionization and K-shell excitation. I. Theoretical model applied to the interpretation of experimental results on H₂O *J. Chem. Phys.* **142** 014307
- [20] Carniato S, Selles P, Andric L, Palaudoux J, Penent F, Žitnik M, Bučar K, Nakano M, Hikosaka Y, Ito K and Lablanquie P 2015 Single photon simultaneous K-shell ionization and K-shell excitation. II. Specificities of hollow nitrogen molecular ions *J. Chem. Phys.* **142** 014308
- [21] Penent F, Nakano M, Tashiro M, Grozdanov T P, Žitnik M, Bučar K, Carniato S, Selles P, Andric L, Lablanquie P, Palaudoux J, Shigemasa E, Iwayama H, Hikosaka Y, Soejima K, Suzuki I H, Berrah N, Wuosmaa A H, Kaneyasu T and Ito K 2015 Double core hole spectroscopy with synchrotron radiation *J. Electron Spectrosc. Relat. Phenom.* **204** 303–12
- [22] Lablanquie P, Penent F and Hikosaka Y 2016 Multi-electron coincidence spectroscopy: double photoionization from molecular inner-shell orbitals *J. Phys. B At. Mol. Opt. Phys.* **49** 182002

- [23] Penent F, Nakano M, Tashiro M, Grozdanov T P, Žitnik M, Carniato S, Selles P, Andric L, Lablanquie P, Palaudoux J, Shigemasa E, Iwayama H, Hikosaka Y, Soejima K, Suzuki I H, Kouchi N and Ito K 2014 Molecular single photon double K-shell ionization *J. Electron Spectrosc. Relat. Phenom.* **196** 38–42
- [24] Hikosaka Y, Lablanquie P, Penent F, Shigemasa E, Eland J H D and Ito K 2010 Two-electron emissions on atomic photoabsorption studied by multi-electron coincidence spectroscopy *J. Electron Spectrosc. Relat. Phenom.* **181** 121–4
- [25] Khalal M A, Lablanquie P, Andric L, Palaudoux J, Penent F, Bučar K, Žitnik M, Püttner R, Jänkälä K, Cubaynes D, Guilbaud S and Bizau J-M 2017 4 d -inner-shell ionization of X e + ions and subsequent Auger decay *Phys. Rev. A* **96** 013412
- [26] Huttula M, Huttula S-M, Lablanquie P, Palaudoux J, Andric L, Eland J H D and Penent F 2011 Spectroscopy of triply and quadruply ionized states of mercury *Phys. Rev. A* **83** 032510
- [27] Bowen I S 1928 Series Spectra of Potassium and Calcium *Phys. Rev.* **31** 497–502
- [28] Bowen I S 1934 The Spectra of Potassium, K IV and K V, and of Calcium Ca V and Ca VI *Phys. Rev.* **46** 791–2
- [29] Kruger P G and Phillips L W 1937 The Spectra of K III, Ca IV, and Sc V, and their Relation to the Spectra of Other Ions in the Isoelectronic Sequence Cl I to Mn IX *Phys. Rev.* **51** 1087–9
- [30] Tomboulia D H 1938 The Spectra of Rb III and Sr IV *Phys. Rev.* **54** 350–4
- [31] Finkelburg W and Humbach W 1955 Ionisierungsenergien von Atomen und Atomionen *Naturwissenschaften* **42** 35–7
- [32] Persson W and Wahlström C-G 1985 Spectrum of Rb IV *Phys. Scr.* **31** 487–505
- [33] Sansonetti J E 2008 Wavelengths, Transition Probabilities, and Energy Levels for the Spectra of Potassium (K I through K XIX) *J. Phys. Chem. Ref. Data* **37** 7
- [34] Sansonetti J E 2006 Wavelengths, Transition Probabilities, and Energy Levels for the Spectra of Rubidium (Rb I through Rb XXXVII) *J. Phys. Chem. Ref. Data* **35** 301
- [35] Pettersen K, Ekberg J O, Martinson I and Reader J 2007 The spectrum of singly ionized potassium, K II *Phys. Scr.* **75** 702–11
- [36] Alna'Washi G A, Lu M, Habibi M, Esteves-Macaluso D, Wang J C, Phaneuf R A, Kilcoyne A L D, Cisneros C and McLaughlin B M 2014 Valence-shell single photoionization of chlorine-like K 2 + ions: Experiment and theory *Phys. Rev. A* **90** 023417
- [37] Liu X-J, Miao Q, Gel'mukhanov F, Patanen M, Travnikova O, Nicolas C, Ågren H, Ueda K and Miron C 2014 Einstein–Bohr recoiling double-slit gedanken experiment performed at the molecular level *Nat. Photonics* **9** 120–5
- [38] Ito K, Penent F, Hikosaka Y, Shigemasa E, Suzuki I H, Eland J H D and Lablanquie P 2009 Application of a simple asynchronous mechanical light chopper to multielectron coincidence spectroscopy *Rev. Sci. Instrum.* **80** 123101

- [39] Anon Cowan R D 1981 *The Theory of Atomic Structure and Spectra* (Berkeley, CA: University of California) ISBN: 978-0-520-90615-0
- [40] Parpia F A, Fischer C F and Grant I P 1996 GRASP92: A package for large-scale relativistic atomic structure calculations *Comput. Phys. Commun.* **94** 249–71
- [41] Fritzsche S 2001 Ratip ? a toolbox for studying the properties of open-shell atoms and ions *J. Electron Spectrosc. Relat. Phenom.* **114–116** 1155–64
- [42] Fritzsche S 2012 The Ratip program for relativistic calculations of atomic transition, ionization and recombination properties *Comput. Phys. Commun.* **183** 1525–59
- [43] Niskanen J, Huttula M, Heinäsmäki S, Schulz J, Urpelainen S, Jänkälä K, Moise A, Alagia M, Avaldi L, Prince K C, Richter R, Aksela S and Aksela H 2009 Core level absorption of laser-excited Rb and Cs atoms *J. Phys. B At. Mol. Opt. Phys.* **42** 175001
- [44] Anon Sugar J and Corliss C 1985 *J. Phys. Chem. Ref. Data* **14** 1–664
- [45] de Bruin T L 1929 Über das zweite Funkenspektrum des Kaliums, K III *Z. Für Phys.* **53** 658–64
- [46] Ekefors E 1931 Vakuumfunkspektren von Kalium und Calcium im Gebiete 100 bis 1100 Å *Z. Für Phys.* **71** 53–88
- [47] Reader J and Epstein G L 1972 Analysis of the Spectrum of Doubly Ionized Rubidium (Rb iii) *J. Opt. Soc. Am.* **62** 1467
- [48] Hansen J E, Persson W and Valind S 1972 On the spectrum of doubly ionized rubidium, Rb III *Phys. Lett. A* **42** 275–6
- [49] Lundqvist M, Baltzer P, Karlsson L and Wannberg B 1994 High-resolution monochromatized He ii α -excited photoelectron spectrum of Ar between 28 and 40.8 eV *Phys. Rev. A* **49** 277–82
- [50] Kikas A, Osborne S J, Ausmees A, Svensson S, Sairanen O-P and Aksela S 1996 High-resolution study of the correlation satellites in photoelectron spectra of the rare gases *J. Electron Spectrosc. Relat. Phenom.* **77** 241–66
- [51] Hall R I, Avaldi L, Dawber G, Rutter P M, MacDonald M A and King G C 1989 Observation of the argon photoelectron satellites near threshold *J. Phys. B At. Mol. Opt. Phys.* **22** 3205–16
- [52] Wilson N J, Hibbert A and Bell K L 2000 Oscillator Strengths for K III, Ca IV and Sc V *Phys. Scr.* **61** 603–10

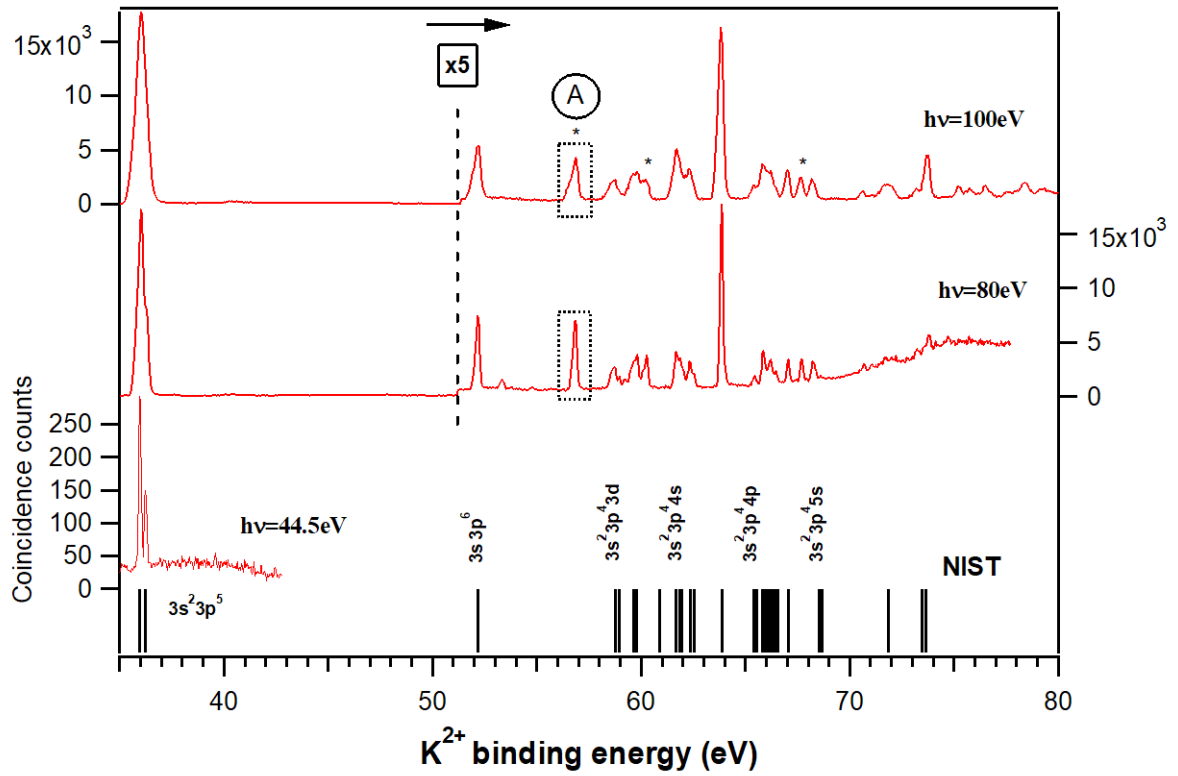


Figure 1 : Histogram of the energy sum of two electrons detected in coincidence recorded at several photon energies. Vertical bars corresponds to K^{2+} energy levels compiled in NIST [1]. The peak labelled A has been assigned to the $3s^2 3p^4(^3P)3d^4D$ state.

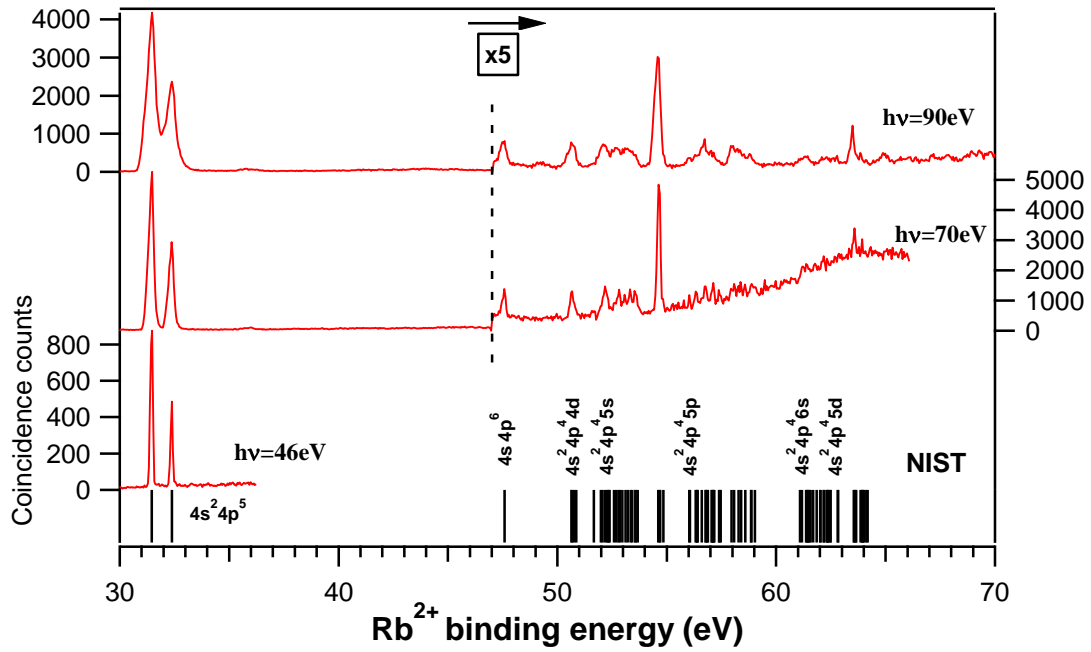


Figure 2 : Histogram of the energy sum of two electrons detected in coincidence recorded at several photon energies. Vertical bars corresponds to Rb^{2+} energy levels compiled in NIST [1].

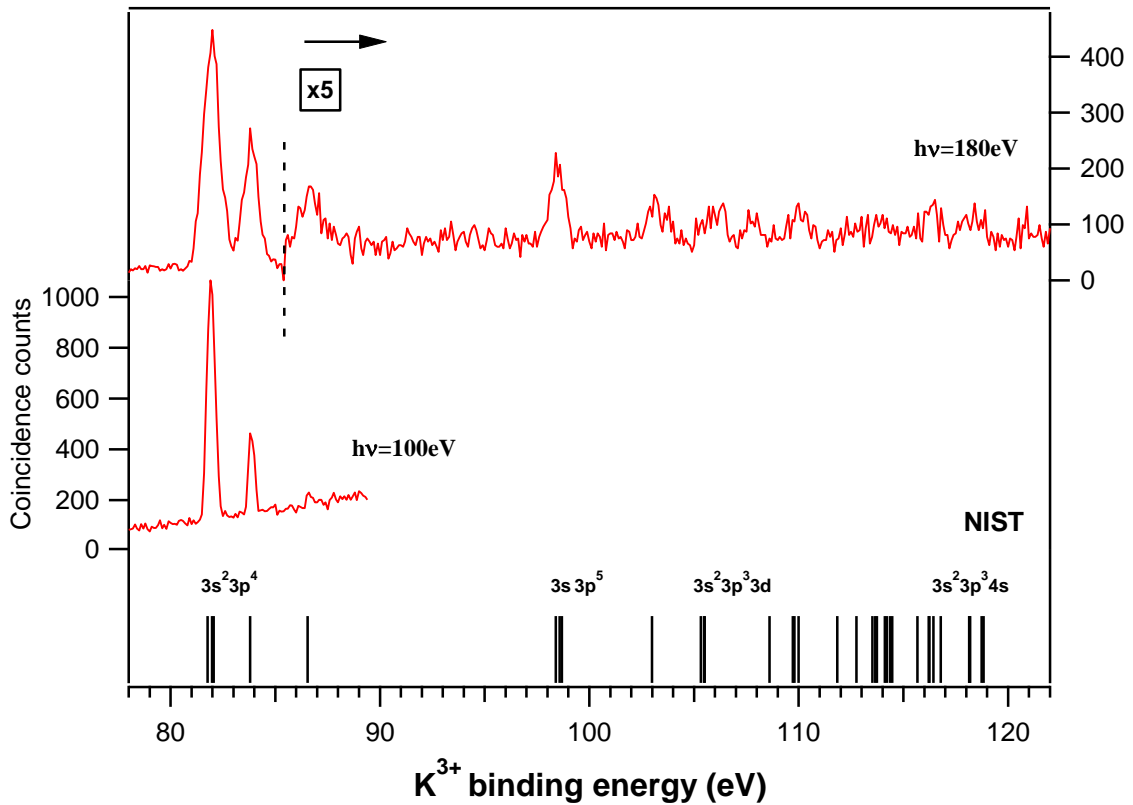


Figure 3 : Histogram of the energy sum of three electrons detected in coincidence recorded at several photon energies. Vertical bars corresponds to K^{3+} energy levels compiled in NIST [1].

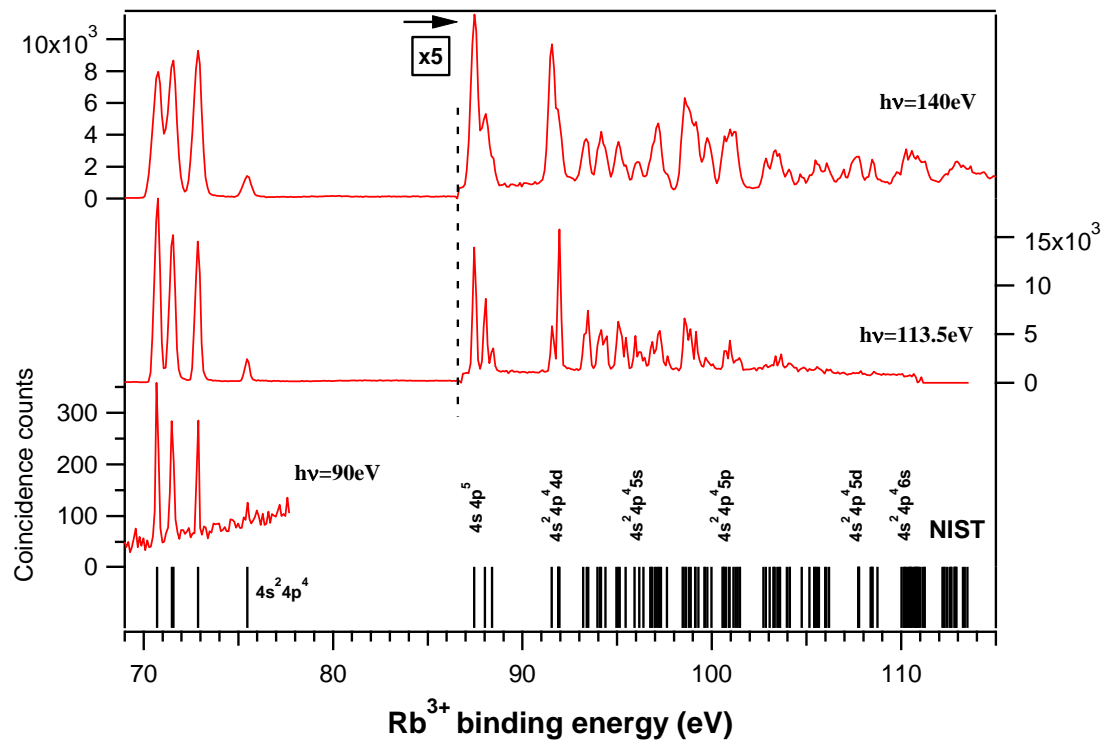


Figure 4 : Histogram of the energy sum of three electrons detected in coincidence recorded at several photon energies. Vertical bars corresponds to Rb^{3+} energy levels compiled in NIST [1].

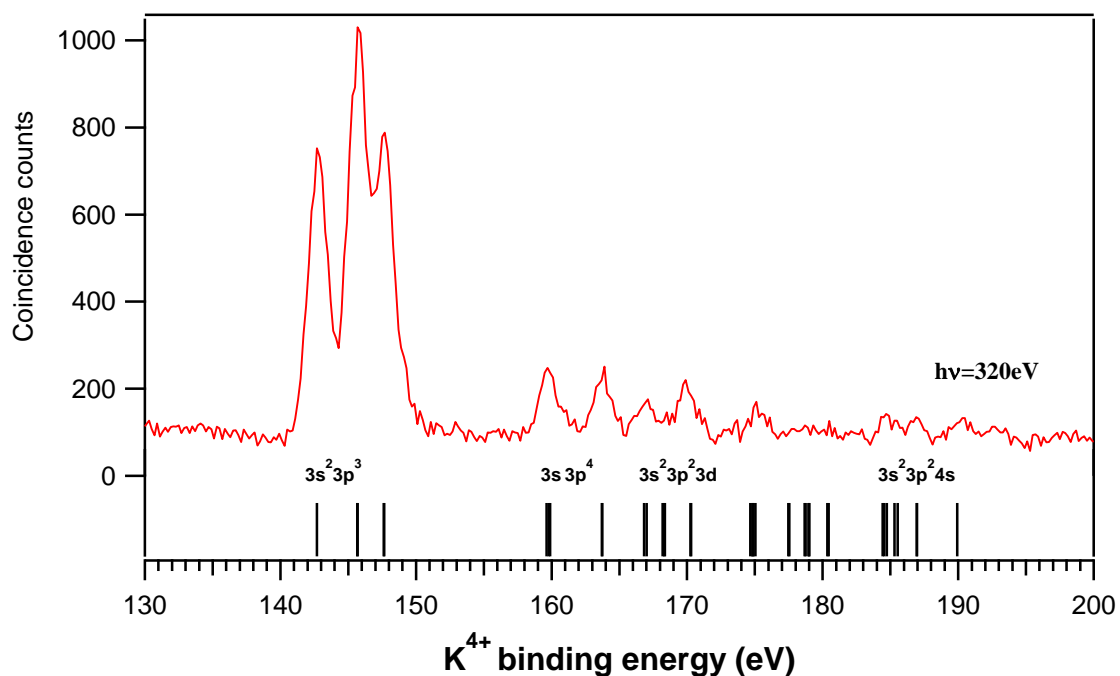


Figure 5 : Histogram of the energy sum of four electrons detected in coincidence recorded at several photon energies. Vertical bars corresponds to K^{4+} energy levels compiled in NIST [1].

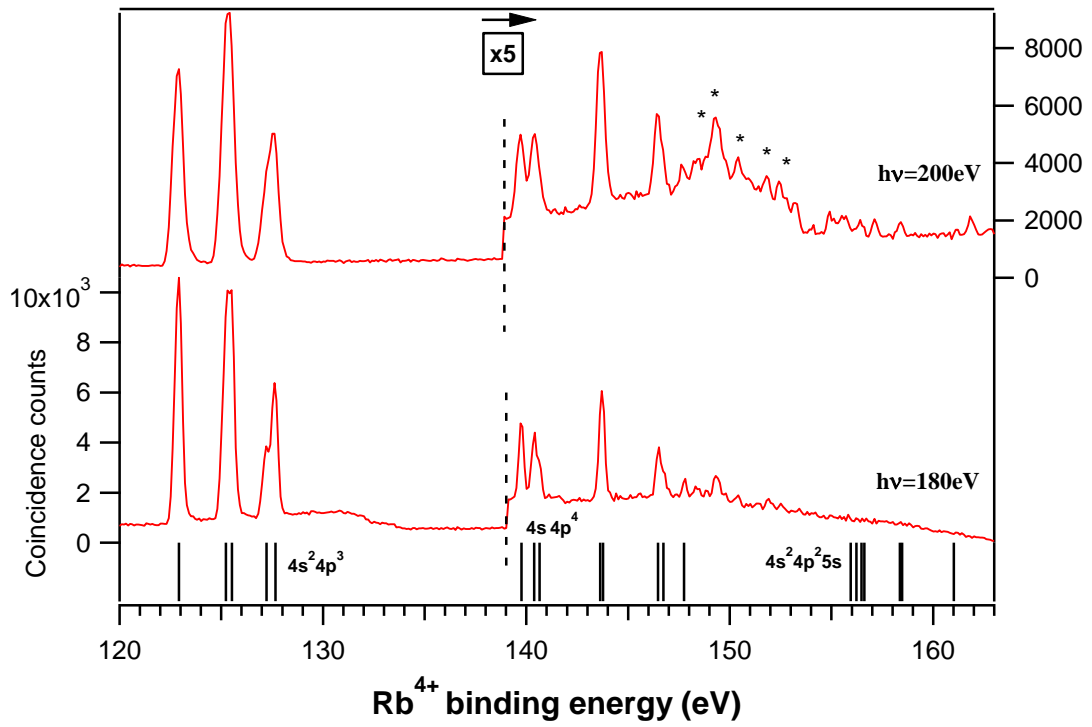


Figure 6 : Histogram of the energy sum of four electrons detected in coincidence recorded at several photon energies. Vertical bars corresponds to Rb^{4+} energy levels compiled in NIST [1].

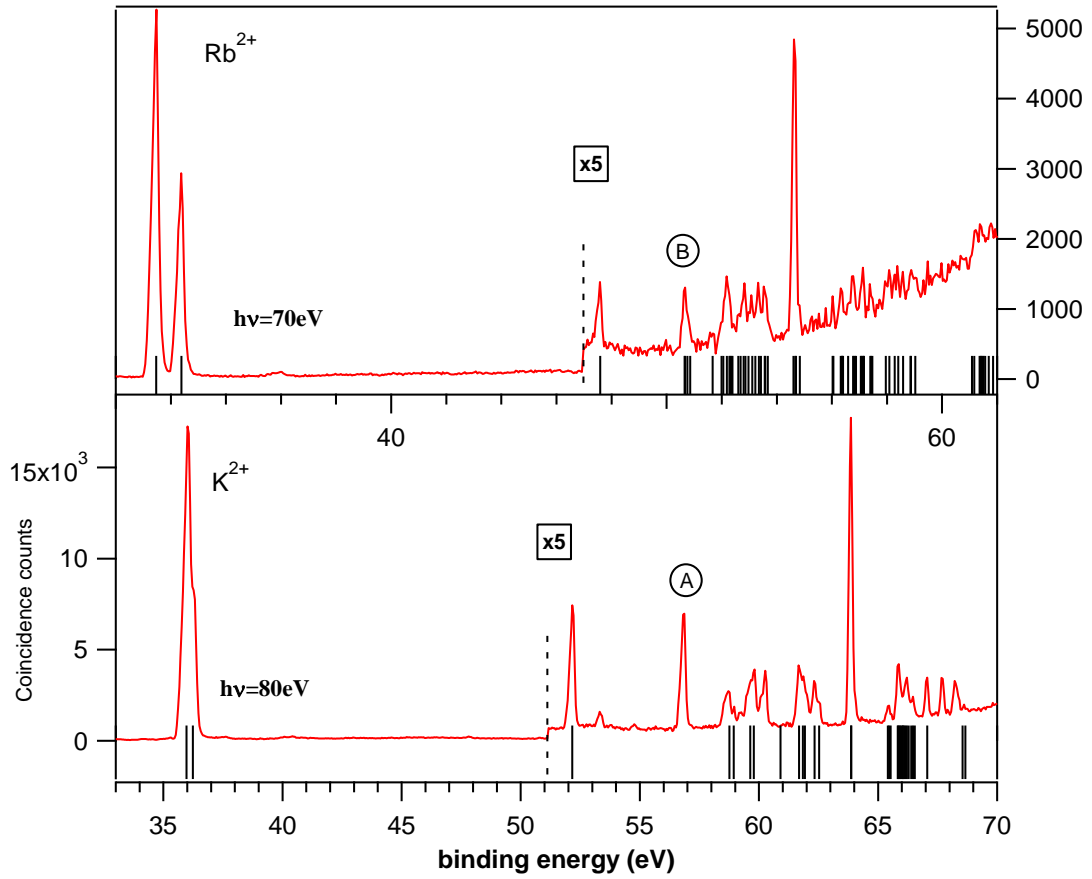


Figure 7 : Histogram of the energy sum of two electrons detected in coincidence for Rb (top) and K (bottom). Vertical bars corresponds to energy levels compiled in NIST [1]. The peak labelled "B" in Rb, which corresponds to the $4s^2 4p^4 (3p) 4d^4 D$ state, is the analogue of the peak labelled "A" in K (not compiled in NIST). We assign the peak A to the $3s^2 3p^4 (3p) 3d^4 D$.

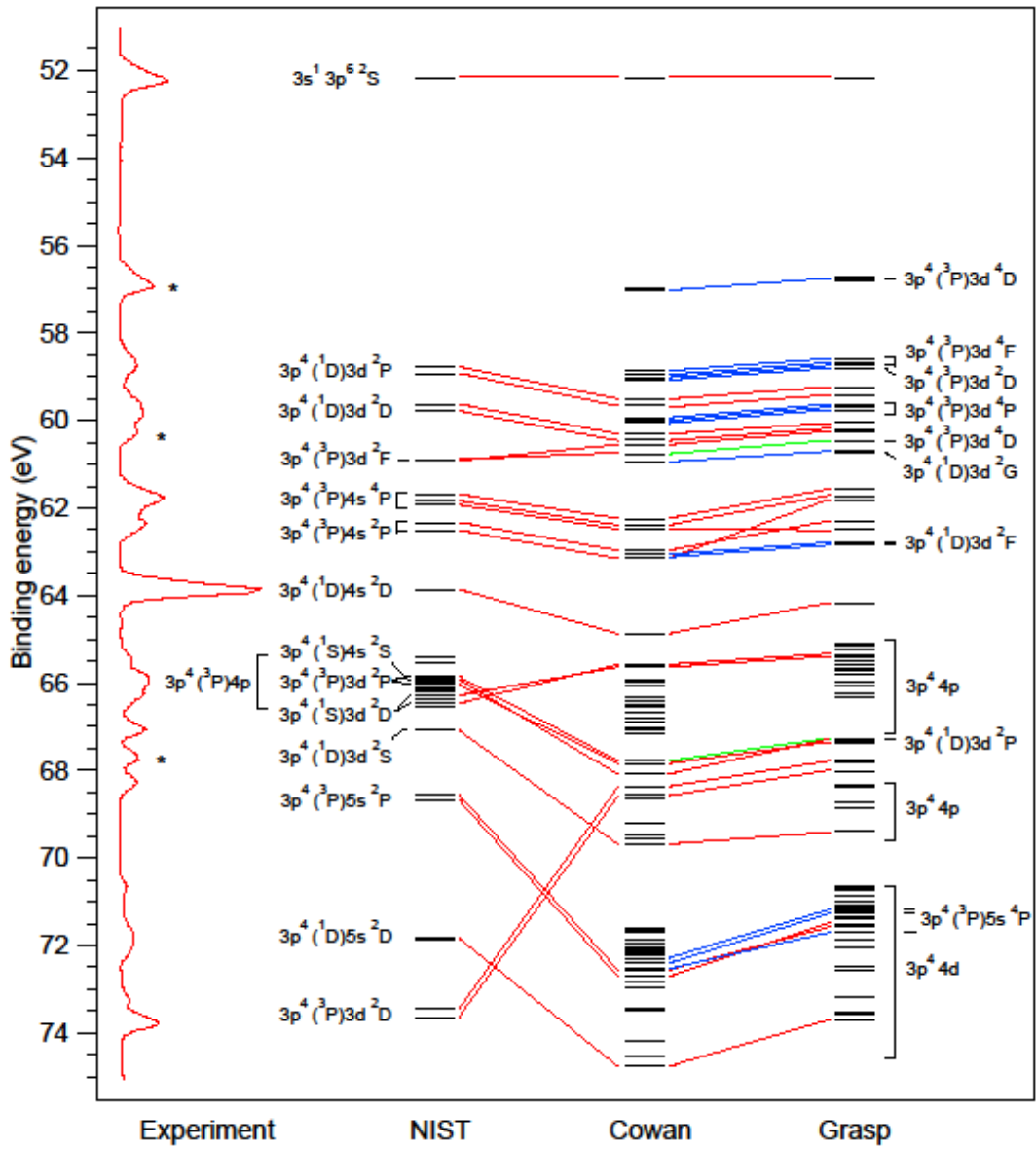


Figure 8 : Assignment of the K^{2+} energy levels. The K^{2+} spectrum is measured at photon energy of 100 eV shown in Figure 1. The predicted binding energies obtained with HF (Cowan) and MCDF (Grasp) schemes are compared with experimental binding energies from NIST [1].