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Final state selection in the 4*p* photoemission of Rb by combining laser spectroscopy with soft-x-ray photoionization

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Fine structure resolved 4p photoemission studies have been performed on free rubidium atoms in the ground state and after excitation into the [Kr]5p $^2P_{1/2}$ and $^2P_{3/2}$ states. The 4$p^5$5p final states have been excited in the 4$p^6$5$s \rightarrow$ 4$p^5$5p conjugate shakeup process from ground state atoms as well as by direct photoemission from laser excited atoms. The relative intensities differ considerably in these three excitation schemes. The differences in the laser excited spectra could be described well using calculations based on the pure jK-coupling scheme. Thereby it was possible to specify the character of the various final states. Furthermore it has been possible to resolve two of the final states whose energy separation is smaller than the experimental resolution by selectively exciting them in a two step scheme, where the laser selects the spin-orbit coupling in the intermediate state and determines the final state coupling after x-ray photoemission.

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I. INTRODUCTION

Fine structure resolved photoelectron spectroscopy on atomic targets is a well established method for studying the quantum mechanical structure of matter. The high energy resolution of third generation synchrotron sources gives detailed insight into the ionic final states of photoionization and thereby reveals precise information on the coupling of core hole states with the valence electrons. Laser spectroscopy on the other hand is a strong tool for specifically exciting optical transitions of the valance electrons and thereby gaining very precise information of the valence shell couplings. In this report it will be shown how a combination of these two methods can strongly enhance the information that can be gained from photoelectron spectroscopy. The detailed knowledge of the underlying atomic effects has been shown to have an impact on the interpretation of similar effects in more complicated materia—like molecules and magnetized solid surfaces [1,2]. Of special interest for these studies are open shell systems where the coupling of the core hole with the valence shell angular momenta gives rise to a rich fine structure in the photoelectron spectra [3].

One of the problems in the interpretation of photoelectron spectra is that the number of final states can be considerably high. Photoelectron spectroscopy provides information on the distribution of the kinetic energy of the photoelectrons, their spin, and their angular distribution. To characterize the final states, additional information on the quantum numbers is important. Here the total angular momentum plays a key role since it is in general the only quantum number that is strictly conserved. While optical measurements give good information about the total angular momentum due to the rigid selection rules of optical transitions, in photoelectron spectroscopy the outgoing electron wave carries away a part of the angular momentum and thus widens the range of possible angular momenta in the final ionic state. Therefore theoretical models must be used to explain the experimental data and provide information on the quantum numbers of the final states. However, the information gained by photoelectron spectroscopy can be increased by combining the technique with laser preparation of the samples. An example for such an experiment is the photoionization of atomic thulium [3]. The set of spectral information could be increased by measuring the linear dichroism of laser polarized free atoms. Hereby more information on the configuration interaction in the final ionic states could be gained.

Another way to combine laser methods with photoelectron spectroscopy is photoemission from laser excited atoms. Photoelectron spectroscopy of laser excited sodium has been performed in the early 1980s by Le Gouët and co-workers [4]. However, the energy resolution of the synchrotron sources had not been sufficient to resolve the fine structure of the atomic lines and third generation synchrotron sources are necessary to study these structures in great detail. Recently Cubaynes and co-workers [5] performed 2p photoemission spectroscopy of 3p excited sodium atoms. They demonstrated a clear dependency of the photoemission intensity from the initial state total angular momentum J_0. In this report we present fine structure resolved 4p photoelectron spectra from laser excited rubidium.

The case of rubidium deviates distinctly from the sodium case by the fact that relativistic effects are much larger leading to a strong spin-orbit splitting of the 4p hole states. Thus the final states of 4p photoionization can be described well within the jK-coupling scheme. The total angular momentum of the core hole couples with the orbital angular momentum of the valence electron to an intermediate quantum number K which couples with the valence electron spin to the total final state angular momentum J_f.

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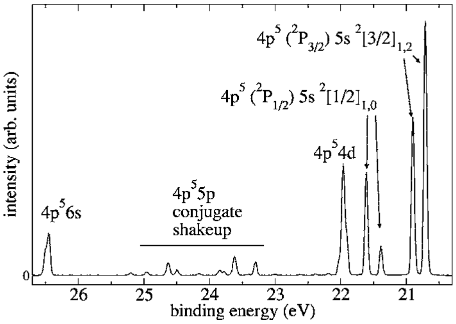

FIG. 1. Overview over the Rb $4p^{-1}$ photoemission spectrum. The spectrum covers the region of the direct photoemission and the $5s \rightarrow 5p$ conjugate shakeup. The assignment is taken from Ref. [9].

II. EXPERIMENTAL SETUP

All spectra have been taken at the undulator beamline I411 of the storage ring MAX II [6,7] in Lund (Sweden). The synchrotron radiation has been monochromatized with a modified Zeiss SX-700 monochromator. A photon energy of 61 eV was used for all spectra. The beam of free rubidium atoms has been prepared by a resistively heated oven at 120 °C producing a stable gas pressure of approximately 10^{-3} mbar in the crucible. The photoelectron spectra were recorded with the equipment [8] built in Oulu, containing a Scienta SES-100 electron spectrometer in the magic angle of 54.7° with respect to the electric field vector of the synchrotron radiation.

For the laser excitation a Coherent 899 ring laser with Ti:Sa crystal as active medium was used in passively stabilized broad band operation. This mode is easy to set up and provides sufficient stability to ensure constant excitation rate of the atoms during the measurements. The laser intensity of about 600 mW focused to a spot smaller than 1 mm^2 was sufficient to saturate the $5s \rightarrow 5p$ transitions at 780.0 nm ($^2P_{3/2}$) and 794.8 nm ($^2P_{1/2}$). The linear polarization of the laser beam has been controlled with a polarizing prism directly before the vacuum viewport.

III. RESULTS

Figure 1 shows the $4p^{-1}$ photoemission spectrum from the rubidium ground state. The four $4p^5 5s$ final states in the binding energy range from 20.3 to 21.8 eV clearly group into two doublets with inner shell total angular momenta $j=1/2$ and 3/2. Beside the direct photoemission lines this spectrum shows several shakeup features. At binding energies close to 22 eV strong lines owing to the excitation of $4p^5 4d$ final states are visible. Between 22.7 and 25.7 eV the $5s \rightarrow 5p$ conjugate shakeup lines and at binding energies above 26 eV the first $5s \rightarrow 6s$ monopole shakeup lines can be seen. The assignment of the lines and the binding energy calibration is taken from optical data [9].

Figure 2 shows the energy range containing the conjugate shakeup lines in detail. This spectrum splits up into two groups of lines for the $4p$-hole total angular momenta $j=1/2$ and 3/2. The coupling of j with the orbital momentum of the valence electron to the quantum number K gives rise to two doublets for $j=1/2$ and three doublets for $j=3/2$. Note that the two lines assigned as $4p^5(^2P_{3/2})5p\ ^2[5/2]_{3,2}$ are only 20 meV separated and cannot be resolved in this spectrum where the total resolution has been determined to be 55 meV full width at half-maximum (FWHM). We will show later in this paper that the combination of laser excitation with synchrotron based photoelectron spectroscopy is a powerful tool to separate this kind of unresolved lines that deviate in their total angular momentum.

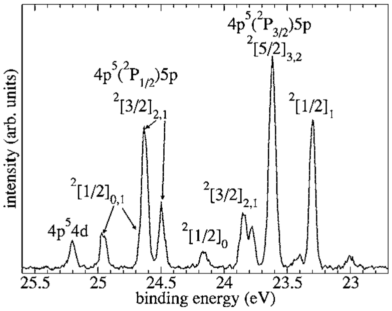

FIG. 2. The $5s \rightarrow 5p$ conjugate shakeup spectrum. The assignment is taken from Ref. [9].

While the $4p^5 5p$ final states shown in Fig. 2 are reached by a shakeup process from the ground state the same final states can also be reached by a two step process including a $5s \rightarrow 5p$ laser excitation followed by direct $4p$ photoemission. The laser can be tuned to excite either the $^2P_{3/2}$ state at 780.0 nm or the $^2P_{1/2}$ state at 794.8 nm.

Figure 3 shows the photoemission spectra from the $^2P_{3/2}$ intermediate state (upper panel) and from the $^2P_{1/2}$ state (lower panel). Owing to the additional energy from the laser photon (1.59 and 1.56 eV), the photoelectrons emerging from the laser excited states show up at lower binding energies than the satellite lines. Because of the fact that only

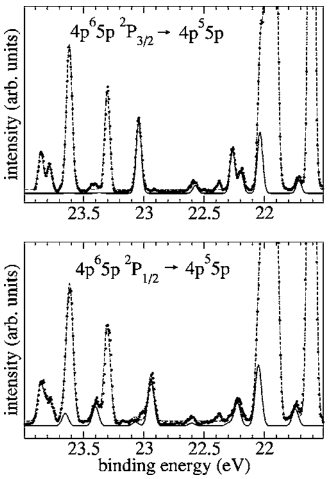

FIG. 3. Comparison of the Rb $4p^6 5p\ ^2P_{J_0} \rightarrow 4p^5 5p$ photoelectron spectra taken from the two different initial states $^2P_{3/2}$ (upper panel) and $^2P_{1/2}$ (lower panel). For each spectrum the dots show the measured photoelectron signal, the dashed lines give a least squares fit containing the structures from the laser-excited and unexcited atoms and the solid curve plots the electron spectrum emerging from laser excited atoms.

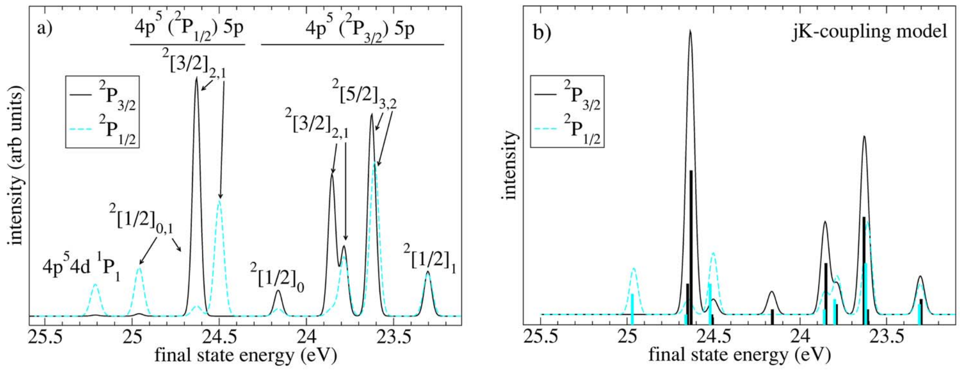

FIG. 4. (Color online) (a) Comparison of the Rb $4p^65p\ ^2P_{J_0}\rightarrow 4p^55p$ photoelectron spectra taken from the two different initial states $^2P_{3/2}$ (black solid line) and $^2P_{1/2}$ (cyan dashed line). The final state energy is given with respect to the ground state of neutral Rubidium atoms. (b) The theoretical spectra assuming pure *jK*-coupling as described in the text. The bars show the relative intensities of the lines (black, $^2P_{3/2}$; cyan, $^2P_{1/2}$) the line spectrum shows a convolution with a 56 meV Gaussian profile.

15%–20% of the atoms can be pumped into the laser excited state, direct photoemission lines as well as the shakeup satellites from the atomic ground state are also visible in the spectrum. To separate the laser excited photoemission a least square fit to all rubidium lines known from optical data [9] has been performed. The dashed line shows the best fit to the data whereas the solid curve shows the photoemission lines from the laser excited ground state. Both spectra have been recorded with linearly polarized laser light. For the $^2P_{1/2}$ state no alignment is possible so that only spectra for parallel electric field vectors of laser light and synchrotron radiation were taken. For the $^2P_{3/2}$ intermediate state the spectra were taken for 0°, 45°, and 90° between laser and synchrotron polarization. The comparison of the spectra showed only very small deviations of the relative intensities with laser polarization. In Fig. 3 the spectrum with parallel electric field vectors of laser light and synchrotron radiation is plotted.

IV. *jK*-COUPLING MODEL

To compare the structures of the photoelectron spectra with different angular momenta in the laser excited state, the fits taken from Fig. 3 have been plotted together in Fig. 4(a). The energy is scaled to the final state energy with respect to the neutral ground state, i.e., the laser photon energy has been added to the measured binding energy. A trend can be seen directly. For each of the doublets denoted with $^2[3/2]$ and $^2[5/2]$ the line of a final state with a lower total angular momentum is more intense in the ionization from the $^2P_{1/2}$ initial state whereas the higher total angular momentum line is more intense in the ionization from the $^2P_{3/2}$ initial state. This finding can be explained by a simple model. The initial states $4p^65p\ ^2P_{1/2}$ and $4p^65p\ ^2P_{3/2}$ differ only in the coupling of the spin to the orbital angular momentum of the valence electron. Under the assumption that the valence electron spin-orbit coupling is not changed during the photoemission it can be stated that the initial state $4p^65p\ ^2P_{1/2}$ should preferably lead to $^2[K]_{K-1/2}$ states whereas $4p^65p\ ^2P_{3/2}$ should preferably lead to $^2[K]_{K+1/2}$ states. This simple argument can be supported by a more accurate estimation of the relative line intensities using the pure *jK*-coupling scheme.

Within the *jK* coupling approximation the relative intensities of the lines from a given initial state can be calculated with the formulas given by Wernet and co-workers [10]. The relative intensities of the fine structure components are given by the coupling coefficients $C_0(j,K_f,J_f)$ which can be obtained by Eq. (15) in Ref. [10]:

$$C_0(j,K_f,J_f) = 3\hat{J}_0^3\hat{K}_f^2\hat{J}_f^2\hat{j}^2(-1)^{J_f+J_0+l_0-1/2}\begin{Bmatrix} j & j & 0 \\ l_0 & l_0 & \frac{1}{2} \end{Bmatrix} \times\begin{Bmatrix} j & j & 0 \\ J_0 & J_0 & J_f \end{Bmatrix}\begin{Bmatrix} J_0 & L_0 & S_0 \\ K_f & J_f & j \end{Bmatrix}^2, \qquad (1)$$

where the standard notation for Wigner 6*j* symbols is used and $\hat{J}\equiv(2J+1)^{1/2}$. L_0, S_0, and J_0 are the quantum numbers of the initial $^2P_{J_0}$ states, *j* is the total angular momentum of the produced core hole and couples with the valence orbital momentum L_0 to the quantum number K_f which couples with S_0 giving the final total angular momentum J_f.

Figure 4(b) gives the relative line intensities as calculated with Eq. (1). The black vertical bars give the heights and positions of the lines emerging from the $J_0=3/2$ initial state. The positions as well as the assignments of the final states have been taken from Ref. [9]. The cyan bars give the intensities for photoemission from the $J_0=1/2$ initial state. These bars are shifted in energy for better visibility. The curves in the same panel have been generated by convoluting the lines with a 56 meV FWHM Gaussian profile.

A comparison of the panels of Fig. 4 shows that the change in relative intensity for most of the doublets can be explained within the *jK*-coupling model. An exception are the excitations of the $4p^5(^2P_{3/2})5p\ ^2[3/2]_{J_f}$ states from the $^2P_{1/2}$ intermediate state. Here the relative intensity of the $J_f=2$ state is overestimated by the theory. This is probably due to a mixing of the three possible $J_f=2$ states. This mixing could be calculated in an intermediate coupling scheme, however, the *jK*-coupling approximation describes the spectra surprisingly well and a more detailed calculation would not lead to deeper insight into the character of the atomic structure. For the $4p^5 4d$ line close to 25.2 eV final state energy no intensity estimation can be given by the model that is limited to the pure $4p^5 5p$ configuration. Despite of these shortcomings of the simple model it describes the observed spectra strikingly well. This shows clearly the value of combining laser spectroscopy with synchrotron based photoelectron spectroscopy. Owing to the high selectivity of the intermediate states by the tunable laser much more information about the process of photoionization can be gained. The assignment of the final state energies to the jK-coupled states can be affirmed and deviations from the pure coupling are directly visible.

V. FINAL STATE SEPARATION

Another strength of the method is visible in the not resolved $4p^5(^2P_{3/2})5p\ ^2[5/2]_{J_f}$ doublet close to 23.6 eV final state energy. The states of this doublet are separated by only 20 meV. Sufficient resolution to resolve these lines can only be accomplished with a painful loss of intensity. However, because the $4p^6 5p\ ^2P_{1/2} \rightarrow 4p^5 5p\ ^2[5/2]_3$ transition is forbidden and the $4p^6 5p\ ^2P_{3/2}$ state photoemission leads preferably into the $4p^5 5p\ ^2[5/2]_3$ final state, photoemission out of laser excited atoms can easily separate these final states.

VI. CONCLUSIONS

The results of the presented report show that photoelectron spectroscopy from laser excited atoms is a promising method for exploring the details of the atomic structure. The angular momentum of the laser excited intermediate state provides a template to map out the available final ionic states and thereby provides additional information that is helpful to identify the final states. The $4p^5 5p$ configuration of atomic rubidium can be described surprisingly well within the jK-coupling scheme. This makes the photoemission of atomic rubidium to a good showcase for the excitation of jK-coupled final states. The usefulness of combined laser and synchrotron spectroscopy for characterizing the final states and for resolving close lying lines has been demonstrated.

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[1] For an overview see S. Svensson, J. Phys. B **38**, S821 (2005), and references therein.
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