

A method to characterize electronic states of 4s ionized Rb by combined laser and synchrotron spectroscopy

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Abstract – Photoelectron studies of laser-excited atomic states can reveal more information about the final ionic states than ground-state photoemission. The possibility to tune the laser to distinct fine-structure sub-states of the excited states allows to select specific angular-momentum couplings of the valence electron that are conserved during photoemission. In the 4s photoemission of laser-excited rubidium we use this method to determine the final-state energies and widths of doubly excited ionic states and characterize the angular-momentum couplings.

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Introduction. – Synchrotron-based photoelectron spectroscopy is a well-established technique to study the electronic structure of atoms, molecules, clusters, and condensed matter. The instrumental resolution of the photoelectron spectrometers and undulator beamlines is under constant improvement. The today available third-generation storage ring beamlines together with state-of-the-art electron spectrometers reach resolutions in the meV range. However, the natural line widths of photoelectron lines is a resolution limit that is difficult to overcome.

Photoelectron spectra are element specific and reveal information of the initial state of matter as well as of the final ionic states of the photoionization process. The width of the spectral lines give additional information of the lifetimes of the final states. In the past it has been evident that better resolution not only results in finer resolution of the known structure, but that so far unknown effects become visible as soon as better resolution is available. However, in atomic and molecular spectroscopy the possibility to resolve new structure comes to a limit as soon as the instrumental resolution becomes better than the natural lifetime broadening. This is specially the case in core hole spectroscopy where the final electronic states decay rapidly via Auger electron emission.

In this article we demonstrate a method to gain more information about the spectral details in photoelectron

spectroscopy by combining fine-structure-resolved laser excitation with high-resolution photoelectron spectroscopy. The laser excitation acts in this experiment as a means to select well-defined electronic couplings of the initial state. This coupling tends to be conserved during the photoemission process [1] and thereby gives additional information about the final ionic states.

Because of their relatively simple electron configuration and the considerable change of angular-momentum coupling scheme from nearly pure LS-coupling for sodium to strong *jj*-coupling for cesium [2], the alkali metals are good model systems for these kind of pump-probe experiments. The first spectra on laser-excited sodium atoms have been taken in the early 80s [3,4] but only recently the spectral resolution of synchrotron light sources and spectrometers became suitable to resolve the fine structure at sufficient count rate to see the weak spectral features caused by laser excitation [5,6].

Experimental setup. – In the presented experiment free rubidium atoms have been produced in a resistively heated oven. A temperature of 120 degrees was sufficient to produce a vapor pressure of 10^{-3} mbar in the crucible. The 5s-electrons were excited into the $5p_{1/2}$ -orbital with a 794.8nm continuous wave Ti:sapphire laser and to the $5p_{3/2}$ -orbital with 780.0nm. While the difference of 14.8nm is a big change for laser light, the corresponding energy difference of 30 meV is difficult to resolve in synchrotron-radiation-based spectroscopy.

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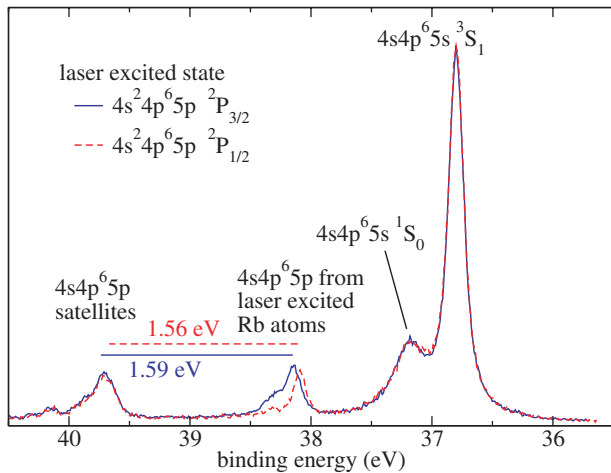


Fig. 1: (Color online) 4s photoemission from laser-excited Rb. In the blue solid spectrum the laser is tuned to the $5s \rightarrow 5p_{3/2}$ excitation. In the red dashed spectrum the $5p_{1/2}$ state has been excited.

The laser-excited and ground-state atoms are photoionized by 60 eV radiation from the I411 beamline of the electron storage ring MAX II in Lund (Sweden). The radiation has been monochromatized using a modified SX700 monochromator [7,8]. The photoelectrons have been analyzed and detected with a modified Scienta SES100 spherical electron spectrometer [9]. The experimental resolution of the combined setup has been determined to be 75 meV by studying the well-known 4p photoemission lines [2].

Results and discussion. – Figure 1 shows the 4s photoelectron spectrum at binding energies between 35.5 and 40.5 eV. This region covers the direct 4s photoemission lines around 37 eV as well as the $5s \rightarrow 5p$ conjugate shake-up lines at 39.5–40 eV. In the single configuration approach using the LS-coupling scheme, two s -electrons can only couple to a singlet state $4s4p^6 5s^1 S_0$ and a triplet state $4s4p^6 5s^3 S_1$. A strong dependence of the lifetime broadening from the spin-spin coupling is visible in these states. The singlet state is considerably broader than the triplet state. To the Auger decay width into the $\text{Rb}^{2+} 4s^2 4p^5^2 P$ states the decay of the 5s-electron into the 4s hole and the emission of a 4p-electron contributes. This process is strong for the singlet state where the spins of the 4s and 5s electrons are antiparallely oriented. For the triplet state this decay can only occur over a less probable spin-flip process. The decay path where a 4p-electron fills the 4s hole and the 5s-electron is emitted is allowed without spin-flip for both couplings and contributes to both line widths.

In the binding energy range between 39.3 and 40.2 eV are the $4s^2 4p^6 5s \rightarrow 4s4p^6 5p + \epsilon s$ satellite structures visible. In the pure LS-coupling scheme these structures should split into a singlet P and three triplet P states. However, owing to the short lifetimes of these states and

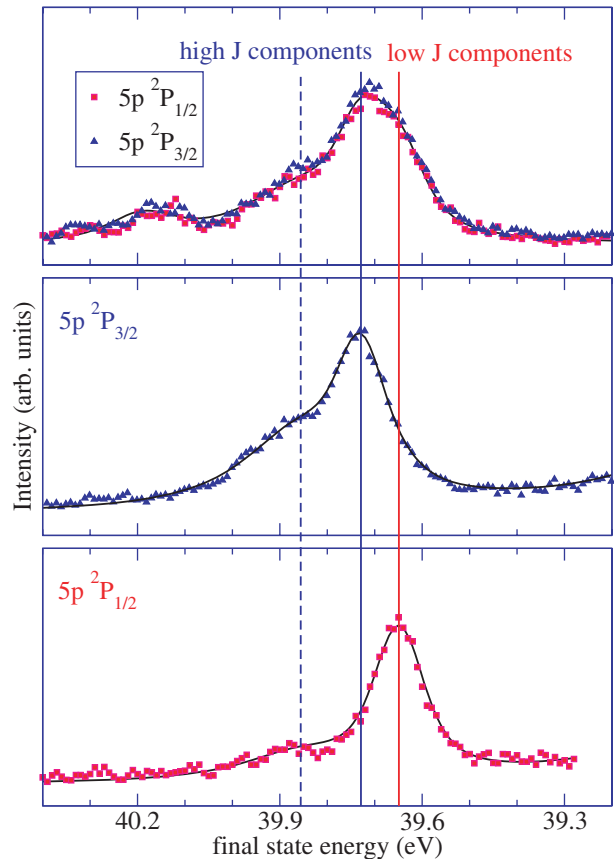


Fig. 2: (Color online) Comparison of the shake-up satellites (upper panel) with the direct 4p photoemission from laser-excited atoms. The energy is given in final-state energy with respect to the neutral ground state. See text for further explanation.

the fact that other configurations such as $4s^2 4p^4 4d 5p$ can contribute to the possible final states, it is not possible to resolve single lines in this spectrum.

The two spectra shown in fig. 1 are taken with the laser tuned to the $5s^2 S_{1/2} \rightarrow 5p^2 P_{1/2}$ (red dashed line) and $5s^2 S_{1/2} \rightarrow 5p^2 P_{3/2}$ (blue solid line), respectively. The spectra are normalized to each other with respect to the top of the most intensive line. The laser excitation gives rise to about 5–10% excited atoms in the sample. The direct 4s photoemission lines from laser-excited rubidium are visible in the binding energy region between 38 and 38.5 eV. The two step process of $5s \rightarrow 5p$ laser excitation followed by direct 4s photoemission leads to the same final states as the $5s \rightarrow 5p$ conjugate shake-up during 4s photoemission from ground-state atoms. This makes it possible to utilize the two step excitation for detailed examination of the final ionic states.

Figure 2 shows the same final states excited by the shake-up process (upper panel), direct photoemission from $5p^2 P_{3/2}$ excited atoms (center panel), and direct photoemission from $5p^2 P_{1/2}$ excited atoms (lower panel). The final-state energy scale is defined by subtracting the measured kinetic energy from the sum of the laser

excitation energy and the synchrotron radiation photon energy. In this energy scale identical final states will be found at the same energies corresponding to the shake-up binding energy.

A direct comparison of the three spectra reveals three distinct structures. The red line marks a structure at lowest final-state energy that is strongly excited from $^2P_{1/2}$ excited atoms and gives a shoulder in the shake-up spectrum. At a final state energy of 39.73 eV the blue solid line marks a second structure that is strong in the $^2P_{3/2}$ laser-excited atoms. Finally the dashed blue line marks a broad structure that is visible in all three spectra but most pronounced in the direct emission from $^2P_{3/2}$ laser-excited atoms.

Studies of the 4p photoemission of laser-excited Rb [1] and the 5p photoemission of laser-excited Cs [10] showed that laser excitation into an initial state with well-defined total-angular-momentum quantum number selects the spin-orbit coupling in the subsequent photoelectron spectrum. Thus, from the observations in fig. 2 it can be directly concluded that the structure marked with the red line mainly consists of final ionic states where the spin of the valence electron is coupled antiparallel to the orbital angular momentum, *i.e.* where the total-angular-momentum quantum number is low ($J=0,1$). The structure marked by the blue line on the other hand must contain ionic states where spin and orbit of the valence electron couple parallelly. These are the high total-angular-momentum components ($J=2$).

In the shake-up satellites the different final states cannot be separated. The low binding energy line is only visible as a shoulder in the whole spectral structure and experimental positions and widths can only be estimated with a considerable uncertainty. Here the method of combining laser combination with photoemission spectroscopy gives new possibilities. Even though the separation of the low-angular-momentum and high-angular-momentum lines is considerably smaller, then their natural line widths, this method allows the experimental determination of both, the line separations and the widths. Additionally the method helps to characterize the momentum couplings of the experimental lines and thereby supports the assignment of the atomic states.

To quantize this observations a least square fit has been made to the three structures observed in the spectra. To minimize the number of free parameters in this fit, all available information about the experiment has been used. Since the three excitation paths, *i.e.* shake-up photoemission and the direct emission from two different excited states, lead to the same final states, the three structures have to have the same splitting and lifetime broadening in all three spectra. From the well-known photon energy of the laser light it is also clear that the laser structures must show binding energies by exactly 1.56 and 1.59 eV lower than the shake-up structure. Finally the Gaussian broadening of the spectrum was known to be 75 meV and could also be fixed in the fitting procedure.

Table 1: Binding energies and Lorentzian widths of the 4s ionized final states from ground-state Rb. Note that the $4s4p^65p$ satellite structures do not consist of single spectral lines but of a mixture of different final states.

Binding energy in eV	Intensity arb. units	FWHM in meV	Assignment
36.80	1.00	118	$4s4p^65s\ ^3S_1$
37.18	0.46	330	$4s4p^65s\ ^1S_0$
39.65	0.05	84	$4s4p^65p\ ^3P\ \text{low } J$
39.73	0.05	71	$4s4p^65p\ ^3P\ \text{high } J$
39.86	0.09	280	$4s4p^65p\ ^1P_1$

Table 2: Binding energies and Lorentzian widths of the photoemission lines from $^2P_{3/2}$ laser-excited Rb.

Binding energy in eV	Final-state energy in eV	Intensity arb. units	FWHM in meV	Assignment
38.06	39.65	0.05	84	$^3P\ \text{low } J$
38.14	39.73	0.57	71	$^3P\ \text{high } J$
38.27	39.86	1.00	280	1P_1

Table 3: Binding energies and Lorentzian widths of the photoemission lines from $^2P_{1/2}$ laser-excited Rb.

Binding energy in eV	Final-state energy in eV	Intensity arb. units	FWHM in meV	Assignment
38.09	39.65	1.00	84	$^3P\ \text{low } J$
38.17	39.73	0.00	71	$^3P\ \text{high } J$
38.30	39.86	0.48	280	1P_1

The results of the fit are summarized in tables 1, 2 and 3.

The least-square fit gives a Lorentzian linewidth of 330 meV for the $4s4p^65s\ ^1S_0$ state and 118 meV for $4s4p^65s\ ^3S_1$. Similarly in the $4s4p^65p$ final states the singlet state is with 280 meV considerably broader than the triplet states (84 and 71 meV). Thus we can state that the widths of the 5p excited final states are also depending strongly on the spin-spin coupling between the 5p-electron and the 4s-electron. However, the $4s4p^65p\ ^{1,3}P \rightarrow 4s^24p^5\ ^2P$ decay of the laser-excited states does not provide a straightforward explanation for the different widths. These experimental findings should be addressed in further theoretical studies including the possible configuration interaction with $4s^24p^4d5p$ states.

The fit also gives the energy separation of the triplet components of 80 meV and between triplet and singlet of 130 meV. These line separations are smaller than the line widths, so that the combination of laser excitation and synchrotron-based photoelectron spectroscopy is the only

method to determine the binding energies and widths of the structures experimentally.

The evaluation of the relative intensities allows to assign the experimental lines to atomic states. In earlier studies of the $4p$ emission from atomic rubidium [1] and the $5p$ emission from atomic cesium [10] it could be shown that photoemission from $^2P_{1/2}$ laser-excited atoms leads preferable to low total-angular-momentum states whereas photoemission from $^2P_{3/2}$ laser-excited atoms leads to high total-angular-momentum states. The structure with final-state energy 39.65 eV is the strongest line for photoemission from $^2P_{1/2}$ laser-excited rubidium and can be assigned to the low- J triplet P states. The line with final-state energy 39.73 eV on the other hand is much more pronounced in the photoemission from $^2P_{3/2}$ laser-excited rubidium. Thus it can be assigned to the high- J triplet P states.

Conclusions. – In conclusion we can state that the method to first excite atoms in a well-defined electronic state and then study the direct photoemission of the excited atoms provides a possibility to study the binding energies and widths of doubly excited final states. With only basic understanding of coupling schemes it is furthermore possible to characterize the angular-momentum coupling of the observed spectral structures. The experimental findings of this article will be a starting point for further theoretical investigation of the final states. It also can be stated that this method is not restricted to the alkali atoms but can be extended to all free atoms and some small molecules that have optical transitions which can be excited with lasers.

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REFERENCES

- [1] SCHULZ J., TCHAPLYGUINE M., RANDER T., BERGERSEN H., LINDBLAD A., ÖHRWALL G., SVENSSON S., HEINÄSMÄKI S., SANKARI R., OSMEKHIN S., AKSELA S. and AKSELA H., *Phys. Rev. A*, **72** (2005) 032718.
- [2] MÄÄTTÄ M., SCHULZ J., HEINÄSMÄKI S. and AKSELA H., *J. Electron Spectrosc. Relat. Phenom.*, **161** (2007) 99.
- [3] LE GOUËT J. L., PICQUÉ J. L., WUILLEUMIER F., BIZAU J. M., DHEZ P., KOCH P. and EDERER D. L., *Phys. Rev. Lett.*, **48** (1982) 600.
- [4] CUBAYNES D., BIZAU J.-M., WUILLEUMIER F. J., CARRÉ B. and GOUNAND F., *Phys. Rev. Lett.*, **63** (1989) 2460.
- [5] CUBAYNES D., MEYER M., GRUM-GRZHIMAILO A. N., BIZAU J.-M., KENNEDY E. T., BOZEK J., MARTINS M., CANTON S., RUDE B., BERRAH N. and WUILLEUMIER F. J., *Phys. Rev. Lett.*, **92** (2004) 233002.
- [6] For an overview, see WUILLEUMIER F. J. and MEYER M., *J. Phys. B*, **39** (2006) R425 and references therein.
- [7] BÄSSLER M., FORSELL J.-O., BJÖRNEHOLM O., FEIFEL R., JURVANSUU M., AKSELA S., SUNDIN S., SORENSSEN S. L., NYHOLM R., AUSMEES A. and SVENSSON S., *J. Electron Spectrosc. Relat. Phenom.*, **101–103** (1999) 953.
- [8] BÄSSLER M., AUSMEES A., JURVANSUU M., FEIFEL R., FORSELL J.-O., DE TARSO FONSECA P., KIVIMÄKI A., SUNDIN S., SORENSSEN S. L., NYHOLM R., BJÖRNEHOLM O., AKSELA S. and SVENSSON S., *Nucl. Instrum. Methods A*, **469** (2001) 382.
- [9] HUTTULA M., HEINÄSMÄKI S., AKSELA H., KUKK E. and AKSELA S., *J. Electron Spectrosc. Relat. Phenom.*, **156–158** (2007) 270.
- [10] SCHULZ J., MÄÄTTÄ M., HEINÄSMÄKI S., HUTTULA M., SANKARI R., KUKK E., RANDER T., SVENSSON S., AKSELA S. and AKSELA H., *Phys. Rev. A*, **73** (2006) 062721.