Intensity Inversion between Main and Satellite Lines in Atomic Photoionization

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The $1s$ photoionization of atomic Li was studied by photoelectron spectroscopy in the photon energy region between 85 and 140 eV for the ground state and the three lowest excited configurations Li* $1s^2n\ell$, $n\ell = 2p, 3s, 3p$. The importance of electron correlations was investigated by comparing the multielectron transitions, so-called shake-up and conjugate shake-up satellites, and the direct process, so-called main lines. The relative intensity of the satellites increases with the level of initial excitation of the Li atom. The shake-up process dominates for states with an $n = 3$ valence electron and the satellites become stronger than the main lines. This spectacular effect can be explained by the spatial overlap of the initial and final state wave functions. Surprisingly, the spatial overlap affects shake-up and conjugate shake-up lines in the same way.

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Photoionization is in general dominated by one-electron processes leading to the ejection of an electron from a particular subshell, when the photon energy exceeds the corresponding electron binding energy. In the electron spectrum, these transitions are observed as strong main photolines. Electron correlations give rise to additional, generally much weaker structures, the so-called satellite lines. This typical behavior characterizes the atomic spectra as well as those of molecules [1,2]. The correct treatment of electron-electron correlations is still a major challenge in the description of photoionization [3–6] and atomic samples serve often as testing ground for the theoretical models of more complex samples. For the satellites, part of the photon energy is used to excite an outer $n\ell$ electron to a different $n'\ell'$ subshell. Transitions without changing the angular momentum of the outer electron ($\Delta\ell = 0$) are commonly understood within a shake-up model, where the intensity of the photolines is directly deduced from the spatial overlap of the electronic wave functions in the neutral and the ionized atom. The intensities for transitions with $\Delta\ell \neq 0$, often labeled conjugate shake-up satellites, are calculated using more sophisticated theoretical approaches (see [7] and references therein). A quite successful framework is the R-matrix code with interchannel coupling effects included explicitly [8,9].

Many experimental and theoretical studies have focused on rare gases and have established the general picture of atomic photoionization [1]. However, experiments on laser-excited Na atoms [10] have shown that a modification of the outer electronic subshell prior to inner shell ionization may lead to an increase of electron correlation, i.e., to an increase in the satellite intensity compared to the photoionization from the ground state. Taking Li atoms as an example, it was predicted theoretically [9,11] that for the photoionization from $3p$ excited states the shake-up satellite lines could become even stronger than the "main" photoline. But no experimental verification of this outstanding, though quite general aspect of photoionization, caused by the strongly different wave functions in the neutral and the ionic states, was available up to now. A systematic study is provided by the present work taking advantage of high brilliance synchrotron radiation sources, intense narrow band ultraviolet lasers and high-resolution electron spectrometers. Atomic lithium was again chosen, since this simple three-electron system is a showcase to study the influence of electron-electron interaction in atomic photoionization [8].

We present here an experimental investigation by photoelectron spectroscopy on the $1s$ photoionization of atomic lithium in the $1s^22s\,^2S_{1/2}$ ground state and in the excited states Li* $1s^22p\,^2P_{3/2}$, $3s\,^2S_{1/2}$ and $3p\,^2P_{3/2}$. The results show a systematic increase of the relative importance of electron correlation when the outer electron is excited successively to higher lying orbitals. An inversion of intensity between the single electron and multielectron transitions occurs already in the ionization of the $3s$ excited state. But the most spectacular effect is found for the Li* $1s^23p$ excited state, where the Li$^+$ $1s4p$ shake-up lines clearly dominate the spectrum. In this way our results confirm the theoretical predictions. In addition, the experimental data enable us to extend the analysis to the discussion of the $\Delta\ell \neq 0$ satellite lines, which, despite a completely different process of production, are affected in a similar way as the shake-up lines by the change of the electronic wave function upon photoionization.

The experiments were performed at beam line UE52/SGM of the synchrotron radiation source BESSY in Berlin (Germany). The counterpropagating laser and synchrotron radiation intersected an atomic lithium beam in the source volume of a high-resolution electron energy analyzer

(Scienta SES-2002). The emitted electrons were measured at the magic angle (54°44′) with respect to the polarization vector of the synchrotron radiation. Laser radiation at 671 nm (see Fig. 1) from a narrow band (1 MHz) cw ring dye laser was used to excite the Li atoms from the Li $1s^22s\,^2S_{1/2}$ ground state to the Li* $1s^22p\,^2P_{3/2}$ excited state. With an output power of 500–700 mW about 20% of the Li atoms in the interaction volume were prepared in the excited state. By tuning the laser to 646 nm and subsequent second harmonic generation in an actively stabilized external ring cavity the excitation into the $3p\,^2P_{3/2}$ state was achieved. With up to 50 mW UV laser light in a bandwidth of 2 MHz about 0.5% of the Li atoms could be excited. According to rate equations, about 10% of these $3p$ excited atoms decay radiatively to the lower lying $3s\,^2S_{1/2}$ state.

The photoionization of the $1s$ shell is not affected by any alignment of the laser-excited states, which might be induced by linearly polarized laser light. This was confirmed by comparing the intensity distribution in the electron spectra after laser excitation to the $3p\,^2P_{3/2}$ state with the spectrum recorded for the unaligned $3p\,^2P_{1/2}$ state. The overall energy resolution of the recorded spectra was measured at a photon energy of 100 eV to be about 65 meV, which comprises the resolution of about 45 meV for both the exciting synchrotron beam and the electron analyzer. The relative transmission of the electron analyzer was determined in each spectrum by normalizing to the known [9] ratio between the Li$^+$ $1s2s\,^1S_0$ main line and the Li$^+$ $1s3s\,^3S_1$ satellite caused by the photoionization of Li atoms in the electronic ground state.

A photoelectron spectrum recorded after laser excitation of the outer $2s$ electron to the $3p$ shell and subsequent photoionization with $h\nu = 100$ eV is given in Fig. 2. Since less than 1% of the Li atoms are excited to the $3p$ shell, the dominant lines arise from the ionization of ground state atoms. In excellent agreement with earlier studies [8], the structures can be attributed to the Li$^+$ $1s2s\,^1S$ and ^3S main photolines and the Li$^+$ $1s3s$ shake-up lines, as well as the Li$^+$ $1s2p$ and $1s3p, 3d$, conjugate shake-up lines. The spectrum arising from the photoionization of excited Li atoms is shown as a zoom of the kinetic energy region between 27.9 and 31.5 eV (Fig. 2, bottom). Here a dramatic change of the ratio is observed. The main lines leading to the Li$^+$ $1s3p$ and $1s3s$ states are no longer the dominant structures, and the Li$^+$ $1s4p\,^1P$ and ^3P satellites exceed by far these main lines.

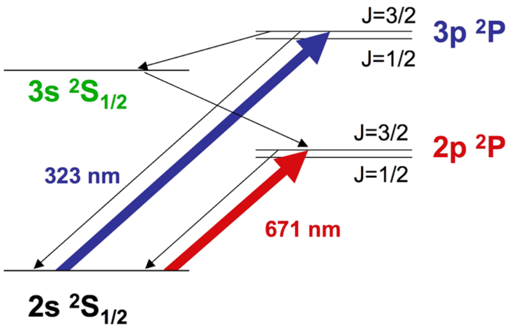

FIG. 1 (color online). Scheme of laser excitation in atomic lithium with electronic ground state $1s^22s\,^2S_{1/2}$ and the subsequent radiative decay pathways.

In the photoionization from the Li $1s^22s$ ground state, the intensity of the $3s\,^{3,1}S$ shake-up transitions comprises about 25% of the direct $1s$ ionization process [9] (Table I). Laser excitation to the $2p$ excited state leads already to an increase of the satellite intensity by a factor of 2 compared to the photoionization from the ground state, but direct photoionization is still the strongest process. This changes after initial excitation to the $n = 3$ orbitals, which leads to an inversion of the satellite to main line ratio. Already for ionization of atoms, which are in the excited $3s\,^2S_{1/2}$ state, the $4s\,^3S$ shake-up line overtops the $3s\,^3S$ main line intensity and the ratio reaches an asymptotical value close to 2. The $4p$ satellites overshoot by a factor of about 5 the $3p$ main lines. These observations prove clearly the theoretical findings [9,11].

The change of the atomic potential when going from the neutral atom to the ion results in a change of the wave functions. This effect is especially large for outer levels carrying an angular momentum, as the difference in per-

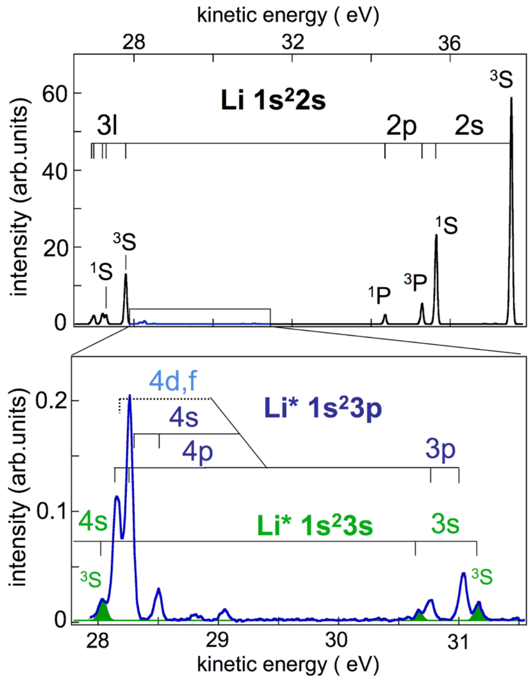

FIG. 2 (color online). Photoelectron spectrum of atomic lithium after laser excitation to the Li* $1s^23p\,^2P_{3/2}$ excited state. The overall spectrum is dominated by the ionization from the ground state (top). Photolines arising from the excited states are seen when the intensity scale in the kinetic energy region 27.9 to 31.5 eV is increased (bottom).

TABLE I. Branching ratios of the $(n+1)\ell$ shake-up and $n\ell$ main line intensities for photoionization at $h\nu = 120$ eV from the Li $1s^2 2s\,^2S$ ground state and the $2p$, $3s$, and $3p$ excited states. Only the intensity of the respective ^3S and ^3P lines are given.

Initial state	2s	2p	3s	3p
Exp.	0.25[a]	0.64(3)	1.8(2)	5.2(5)
Theory [9]	0.25	0.65	⋯	5.4

[a] The 2s ground state was used to normalize the experiment to theory.

ceived central charge is maximal there. A simple model using the formula for the mean radii of hydrogenlike systems shows the proximity of the atomic $3p$ orbital with a radius of $12.1a_0$ and the ionic $4p$ with $11.3a_0$, in contrast to a value of $6.1a_0$ for the radius of the ionic $3p$. So the $3p$ wave function of the neutral laser-excited atom is much closer to the $4p$ than to the $3p$ wave function in the ion, giving rise to the dominance of the satellite lines. This finding is similar to the situation observed upon resonant inner shell excitation [12,13], where shake-up processes dominate the resonant Auger decay.

The energy dependence of the branching ratio between the shake-up satellites (SU) and the main photolines (ML) shows a decrease of the satellite intensity when the photon energy approaches the Li^+ $1snp$ ionization thresholds (Fig. 3). This tendency is well known and nicely reproduced by R-matrix calculations [9]. In a simple picture this effect arises from the fact that only far above threshold the overlap between the neutral and the ionic wave functions can be considered as constant (sudden approximation). Closer to threshold the interaction between the outgoing electron and the remaining core has to be taken into account causing a more adiabatic relaxation and thereby a higher main line intensity [7]. Nevertheless for all photon energies the shake-up intensity for ionization of the Li^* $1s^2 3p\,^2P_{3/2}$ excited state clearly exceeds the intensity of the so-called main line.

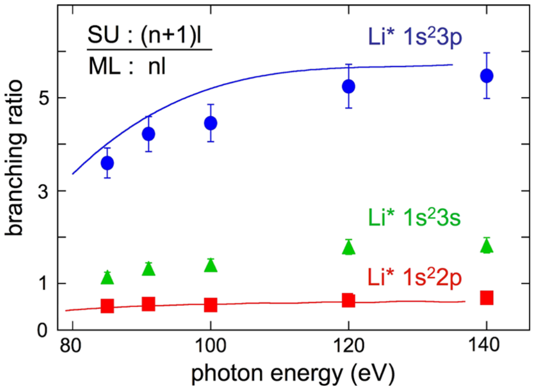

FIG. 3 (color online). Branching ratio between the $(n+1)\ell$ shake-up satellites and the $n\ell$ main photolines after photoionization from the Li^* $1s^2 2p\,^2P_{3/2}$, $3p\,^2P_{3/2}$ and $3s\,^2S_{1/2}$ excited states. The theoretical curves obtained by R-matrix calculations [9] are given as solid lines for comparison.

Since the parity of the residual ion is different for shake-up and conjugate shake-up (CSU) lines, also the underlying mechanism must be different. Consequently, the term "conjugate shake-up satellite" is sometimes challenged, in order to avoid a too close analogy with the regular shake-up process [8]. We still use the term here, as it is widely used in the community, but we do not imply any underlying mechanism by that name. The difference between SU and CSU becomes apparent in Fig. 4 (top), where the energy dependence of the Li^+ $1s(n+1)s\,^3S$ satellites for ionization from the Li^* $1s^2 np\,^2P_{3/2}$, $n = 2, 3$ laser-excited states is depicted. Both the $n = 2$ and $n = 3$ CSU show in contrast to the SU an increase of their intensity relative to the main line, when the photon energy approaches the ionization threshold. This is in agreement with all theoretical treatments for these satellite lines [8].

Although the underlying processes related to SU and CSU satellites are different, our results show a close similarity between the two for the investigated photoionization of excited states concerning their n-dependence (bottom panel of Fig. 4). When the CSU to SU ratio is plotted against the photon energy, there is virtually no difference in the curves for $n = 2$ and $n = 3$. This strongly suggests that the overlap of the atomic and ionic wave functions affects

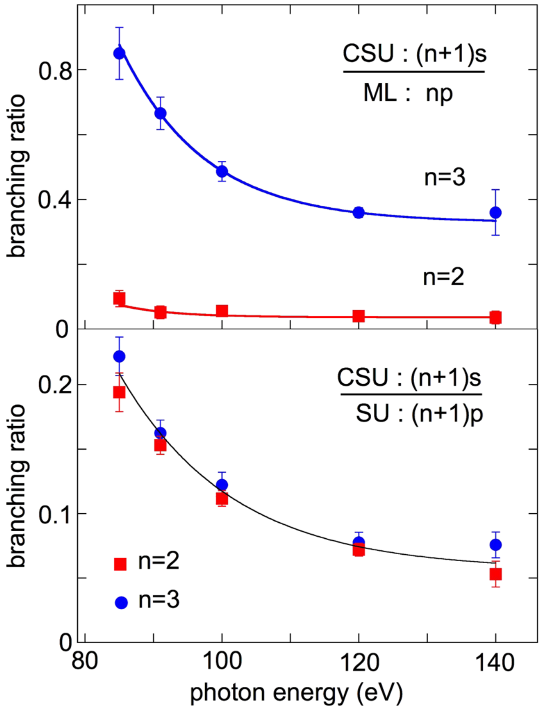

FIG. 4 (color online). Branching ratio between the CSU $(n+1)(\ell-1)$ satellite and the $n\ell$ main photolines after photoionization from the Li^* $1s^2 2p\,^2P_{3/2}$ and $3p\,^2P_{3/2}$ excited states (top). CSU to SU branching ratio (bottom).

the CSU process in the same way as it does affect the normal shake process. We would like to point out that we are discussing CSU lines with $\Delta\ell = -1$ here. For alkali atoms only CSU satellites with $\Delta\ell = +1$ are possible from the ground state [9,14]. There is, however, no evidence that this difference has fundamental impact on the connected processes. The $\Delta\ell = +1$ satellites originating from the excited states in our experiment were not well enough resolved for a solid quantitative analysis.

To further our understanding of the similar energy dependence of the SU and CSU satellites branching ratio, we employ a simplified model. In this picture, the cross sections for the processes involved can be derived by calculating the absolute squares of the following set of matrix elements (applied to the cases discussed here):

$$\begin{aligned} \text{ML: } & \langle 1s|r|\epsilon p\rangle\langle np|np\rangle, \\ \text{SU: } & \langle 1s|r|\epsilon p\rangle\langle np|(n+1)p\rangle, \\ \text{CSU: } & \langle 1s|\epsilon s\rangle\langle np|r|(n+1)s\rangle. \end{aligned}$$

All matrix elements have atomic wave functions to the left and the ionic wave functions on their right hand side. Both the ML and the SU feature a $1s \rightarrow \epsilon p$ dipole transition and a monopole (spatial overlap) matrix element for the bound-bound transition between atomic and ionic states. This is reversed for the CSU, where the dipole matrix element connects the bound states and a monopole transition represents the ionization process. Consequently, the CSU/SU branching ratio is given by the absolute square of the product

$$\frac{\text{CSU}}{\text{SU}} : \frac{\langle 1s|\epsilon s\rangle}{\langle 1s|r|\epsilon p\rangle} \frac{\langle np|r|(n+1)s\rangle}{\langle np|(n+1)p\rangle}.$$

As above, the first factor describes the creation of the core hole and the second one the excitation of the valence electron. The first factor with the direct dependency on the outgoing electron's kinetic energy ϵ is the same term that would be used in the calculation of the CSU/ML branching ratio. The behavior for different values of n can be derived from the second factor only. In a first order approximation this ratio can be considered as constant with varying n, which is in agreement with our experimental results in Fig. 4. Although we have used a quite simple model, which is known to fail for the calculation of absolute values for the satellite intensities, it brings out the general trend in our observation: The SU and the CSU satellites are affected in the same way by the change of atomic orbitals during photoionization because there is no difference between monopole and dipole transitions in this respect.

In conclusion, we have shown that the intensity ratio between satellite and main lines in the direct photoionization is strongly affected by the initial preparation of the atom. Effects of electron correlations, which cause the satellite intensities, are becoming more important for the ionization of excited states. In the case of photoionization from Li atoms laser-excited to the $3p\,^2P_{3/2}$ state the strong difference between the wave functions in the neutral and ionic state makes even the usual identification of main and satellite lines misleading, since the satellite becomes by far the strongest feature. In this way, our experiments confirm earlier theoretical results, but call also for further developments, in particular, for the interpretation of the intensity of the conjugate shake-up lines, which show close similarities to the shake-up lines in their dependence from the principal quantum number n occupied in the initial state.

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