Auger decay of the 3d hole in the isoelectronic series of Br, Kr+, and Rb2+

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The Auger decay process of the 3d½ hole is studied experimentally and theoretically along the isoelectronic Br, Kr+, and Rb2+ series with electron configuration [Ar] 3d⁶4s²4p⁶. The experimental results consist of multielectron coincidence data measured from all three elements and conventional high-resolution Auger spectrum for the Br case. Theoretical interpretation was done by using multiconfiguration Dirac-Fock calculations. It is found that the decay rate of two-Auger-electron emission increases along the series in the direction of decreasing nuclear charge. Also, complexity of the Auger spectrum follows the same trend, requiring a drastic increase to the size of the configuration space for describing the observed spectra.

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I. INTRODUCTION

Shallow inner-shell atomic holes are excited states that decay predominantly by release of a so-called “Auger electron” [1,2]. However, a weaker, “double-Auger” decay path, in which two Auger electrons are emitted, was discovered at the end of the 60s in Ne and Ar atoms [3,4]. The improvement of electron coincidence experiments brought deeper insight into this process, enabling the detailed study of the ways the double-Auger decay can proceed: through a series of decays called cascade Auger decays or through a direct process [5–8].

This direct double-Auger decay, in which the two Auger electrons are simultaneously emitted, has a lower probability but is a direct manifestation of a three-electron correlation process. Its detailed study took more time, for both experiments [6] and theory, which refers to knock-out and shake-off mechanisms [9,10]. More recently experimental evidence for a direct triple-Auger decay has also been found in C⁺ ions [11] and Ar atoms [12].

In this work, we have studied the Auger decay of the 3d holes in the isoelectronic configuration [Ar] 3d⁹4s²4p⁶ in the cases of Br, Kr+, and Rb²+. We present here only the decay of the 3d½ component, as the two 3d j spin-orbit components (j = 3/2 or 5/2) behave in a similar way. The main decay of a 3d½ hole happens through an M₄,5N/N Auger path which has been studied extensively in Kr+ over the time of five decades [8,13–17]. These studies have, among other things, shown that the decays of the 3d½ hole can proceed through a cascade Auger decay with a ∼29% probability [8]. A question arises whether a similar behavior follows the 3d½ hole decay in an isoelectronic Br atom and in a Rb²+ ion. More precisely, the question is to study the influence of the change in core charge, increasing from Br to Kr+ and to Rb²+, on the Auger decay. To the best of our knowledge, no information is available in the literature for the Rb²+ 3d⁹4s²4p⁶ system, except for a Ph.D. thesis [18]. As for the Br atom, the 3d photoabsorption was investigated in Refs. [19,20] and the decay of the (3d → 4p) resonance was studied theoretically and experimentally by photoelectron spectroscopy [21], suggesting a dominant decay into singly ionized Br⁺ states. However, no detailed information of the Auger decay pathways has been available.

As bromine is highly reactive in atomic form, the Br 3d⁻¹4s²4p⁶ states are created via ultrafast dissociation of the HBr molecule upon HBr (3d−1 → σ∗) photoexcitation [22]. The observed process can be described as

\[ hv + HBr \rightarrow HBr(3d^{-1} \rightarrow \sigma^*) \rightarrow H + Br(3d^{-1}1p^6). \]

Note that the ultrafast dissociation of the HBr (3d → σ∗) resonance is the dominant process, and it occurs in competition with the weaker autoionization paths within the HBr molecule (see Ref. [23] and the references therein for details).

The single- and double-Auger decays of 3d holes have been measured by electron spectroscopy after 3d excitation or ionization using synchrotron radiation and interpreted with theoretical predictions obtained from multiconfiguration Dirac-Fock calculations.

II. EXPERIMENT

The study used two experimental setups: the first was a multielectron coincidence spectrometer, the magnetic bottle.
electron time-of-flight spectrometer HERMES [8,12]. It provides an energy resolution $\Delta E/E$ of $\sim 1.6\%$, where $E$ is the kinetic energy of the electron. The second was a high-resolution hemispherical electron energy analyzer (MBS-A1) [23]. Its resolution was $\Delta E$ 20 meV, including the contribution of the analyzer (12 meV) and of the Doppler broadening (10 meV). The axis of the electrostatic lens of the analyzer was perpendicular to the photon beam and fixed at the magic angle (54.7°) relative to the direction of polarization of the incident synchrotron radiation.

The experiments on Kr and Rb were performed at the undulator beamline PLEIADES [24] of the SOLEIL synchrotron facility during the single-bunch operating mode of the synchrotron, providing bunches of light every 1184 ns. The Auger decay of the Kr$^+$ $3d_{5/2}^{-1}4s^24p^6$ states were obtained by analyzing coincidences with a $3d_{5/2}$ photoelectron, in a similar way as was done by Palaudoux et al. [8]. The Auger decay of the Rb$^{2+}$ $3d_{5/2}^{-1}4s^24p^6$ states involved a more complex analysis, in which the Auger electrons were identified by their detection in coincidence with the pair of $3d$ and $5s$ photoelectrons. Such a procedure was previously developed to study the Auger decay of the Ar$^{2+}$ $2p^{-1}3s^23p^3$ states [25] and applied to the study of the decay of the 4d hole in the Xe$^+$ ion [18,26].

The excited Br $3d_{5/2}^{-1}4s^24p^6$ state was created through ultrafast dissociation of the HBr molecule upon $(3d \rightarrow \sigma^*)$ excitation [22]. Its Auger decay was obtained using the multielectron coincidence setup HERMES at the undulator beamline U56/2 PGM2 [27] of the BESSY-II synchrotron radiation facility in Berlin, Germany. The synchrotron was used in single-bunch operation mode, providing bunches of light every 800.5 ns. Figure 1 displays the Auger spectra measured on the HBr $(3d_{5/2} \rightarrow \sigma^*)$ resonance. The raw spectra contain the contribution of the multiple ionization of the HBr molecule. The Auger decay of the atomic Br $3d_{5/2}^{-1}4s^24p^6$ state is obtained by subtracting an off-resonance spectrum. This is illustrated in Fig. 1(a), in which the on- and off-resonance, total one-dimensional Auger spectra are shown. The difference gives the contribution of the Br atomic Auger decay and is displayed in Fig. 1(b). It compares well with the Auger spectrum obtained with the same method by Morin and Nenner [22] and the one obtained directly on Br atoms, obtained by laser dissociation of the Br$_2$ molecule by Nahon et al. [21]. In a similar way the raw two-dimensional energy correlation map of electron-electron coincidences measured at the HBr $(3d_{5/2} \rightarrow \sigma^*)$ resonance is displayed in Fig. 1(c). Integration along the diagonal lines gives the final dicaticonic states shown in Fig. 1(e). The contribution associated with the double ionization of the HBr molecule is estimated off-resonance. Its subtraction gives in Fig. 1(d) the population of the Br$^{2+}$ states populated upon double-Auger decay of the Br $3d_{5/2}^{-1}4s^24p^6$ state.

Finally a high-resolution conventional Auger spectrum of the Br $3d_{5/2}^{-1}4s^24p^6$ state was obtained with the MBS-A1 analyzer at the soft x-ray beamline BL6U at the UVSOR facility at the Institute for Molecular Science in Okazaki, Japan [23]. It is presented in Fig. 2(b). As in the previous experiment, it was obtained using the ultrafast dissociation of the HBr molecule upon $(3d_{5/2} \rightarrow \sigma^*)$ excitation. The same procedure as in Fig. 1(a) is used in Fig. 2(a) in order to extract the atomic contribution shown in Fig. 2(b). It compares well with the lower-resolution Auger spectra obtained previously [Fig. 1(b) or 2(c)]. The spectrum has been calibrated in energy by adopting the method used in Ref. [23], which places the 4s$^2$4p$^3$ $^{1}P$ Auger line at 38.42 eV. Note that weak shadow peaks [marked with asterisks in Fig. 2(b)] are observed at a higher kinetic energy above the main Auger peaks; they are assigned...
to the other spin-orbit component, that is, to the decay of the Br $3d_{5/2}$:4$s^2$4$p^6$ state, because the $(3d_{5/2} \rightarrow \sigma^*$) resonance can be weakly excited at the photon energy of 70.7 eV, on top of the HBr $(3d_{5/2} \rightarrow \sigma^*)$ resonance. These spurious peaks appear at about 1.04 eV above the main Auger peak, a value in agreement with the Br $3d$ spin-orbit splitting measured by Nahon et al. [21].

### III. CALCULATIONS

Theoretical simulations were carried out using the multi-configuration Dirac-Fock (MCDF) method with the Flexible Atomic Code (FAC) [28] and GRASP2K [29,30] to acquire predictions for the Auger decays in the studied isoelectronic series. The atomic states were obtained by diagonalizing the Dirac-Coulomb Hamiltonian matrix in the basis of $jj$-coupled antisymmetric configuration state functions of the same total angular momentum, projection, and parity.

In each of the isoelectronic cases, simulation with FAC was run in two parts: the first part featuring the initial decay of the 3$d$-hole state into the intermediate states, and the second part featuring the subsequent Auger decay of those intermediate states into their final states. During the first part of the simulation the configuration $3d^2 4s^2 4p^6$ is used to describe the initial 3$d$-hole state. The intermediate states (final states of the first part) are described by a set of configurations: $4s^2 4p^6$, $4s^2 4p^4 4p^2(5s, 4/5/6d^2)$, $4p^4 4d^0$ $kd$, $4s^2 4p^5(5s, md)$, $4/5s np^5$, $np^3 md$, $4s^2 np^3(5s, md)$, $4s^2 4p^2 lp^2(5s, md)$, $4/5s 4p^2 l p^2$, $4/5s 4p lp^4$, $4p^3 lp^2 md$, $4p lp^2 md$, in which $n = 4, 5, 6, 7, 8$, and 9; $\ell = 5, 6, 7, 8,$ and 9 and $k = 5, 6, 7, 8$, and 9 (total of 32 480 states). The simulation of the decay into the states consisting of these configurations was run separately for even- and odd-parity cases.

Simulation of the second Auger decay was performed to obtain theoretical estimates for the lifetimes of the intermediate states, namely, the final states in the first step of the decay process. The final states (of the second step of the decay process) consist of configurations $4s^2 4p^4$, $4s^2 4p^2(5s, 4/5/6d)$, $4s^2 4p(5s, 4/5d)$, $4s^2 4p(5s, 4/5d, 4d^2, 4d^4)$, $4p^4$, $4s^2 4p^2(5s, 4/5d)$, $4p^2(5s, 4/5d, 4d^2, 4d^4)$, and $4p^2(5s, 4/5d, 4s^2)$ (total of 1965 states). The calculated lifetimes contribute to the width of the peaks observed in the Auger spectrum seen in Fig. 2(d).

In order to get a more comprehensive understanding of the Auger processes at hand, they were also simulated with GRASP2K together with the RATUP suite [31,32]. Because of the limitations imposed by GRASP2K and to achieve convergence, a more limited configuration space was used. The initial 3$d$-hole state was described by $3d^3 4s^2 4p^6$, and the intermediate states consisted of configurations $4p^6$, $4s^2 4p^4$, $4s^2 4p^2(4d^2, 5s^2, 4d^5)$, $4s^2 4p^5(5s, 4/5/6d)$, and $4s^2 4p(5s, 4/5/6d)$ (total of 668 states). The states of the final step were described by configurations $4s^2 4p^3$, $4s^2 4p^2(5s, 4/5/6d)$, $4s^2 4p^2$, $4s^2 4p^3 4d$, $4s^2 4p^2 4d^2$, and $4p^5$ (total of 390 states).

### IV. DISCUSSION

We present here the decay of the $3d_{5/2}$ hole only, as the two $3d_j$ holes behave in a similar way. For the Kr and Rb cases this selection is enabled by using the multielectron coincidence technique, which provides a direct way to isolate Auger spectra from different initial ionic states.

The Auger spectra of the decay of the $3d_{5/2}$ hole in the isoelectronic series of atomic Br, Kr$^+$, and Rb$^{2+}$ resemble each other, but interestingly also notable differences are observed. We show that the evolution of various equivalent line groups and the total intensity distribution within the series can be followed as a function of the atomic number Z. All the intermediate and final atomic states in the series are very sensitive to configuration mixing in the MCDF scheme, which
is the reason for some of the discrepancies in labeling in contrast with some earlier studies [8,16] as well as within the series regarding the leading configuration.

The 3d/2 Auger spectrum in Br is the one we investigated experimentally in finer detail. Therefore, its assignment is discussed first, comparing it with the earlier work on the isoelectronic Kr+ counterpart [8,16]. We then describe the trends observable in the isoelectronic series of Br, Kr+, and Rb2+.

A. Auger decay of the 3d/2 hole in Br

The \( j = \frac{5}{2} \) component of the high-resolution Br \( M_{4,5}NN \) Auger spectrum collected with the hemispherical electron energy analyzer (MBS-A1) at BL6U is presented in Fig. 2(b). It is compared with the lower-resolution spectrum obtained with the magnetic bottle spectrometer in Fig. 2(c). Comparison with the equivalent Auger spectra of the isoelectronic Kr+ and Rb2+ in Fig. 3, and reference to the energy levels in Fig. 4, allows one to recognize the main features of the experimental Br Auger electron spectrum.

Starting from the higher kinetic energy side in Fig. 3, between 53 and 49 eV is a feature arising from decays to Br+ 4s24p\(^6\) levels, between 41 and 38 eV is a feature corresponding to 4s4p\(^5\) final states, and at 26.6 eV is a line corresponding to \( 4p^04p^0 \) decay. In the following these configurations are labeled as e, d and a, respectively.

In addition to the main groups, the spectrum consists of many lines that are due to electron correlation (i.e., final-state configuration mixing). The calculations shown in Fig. 2(d) give their assignments. The first remark is the strong configuration mixing that is necessary to reproduce the spectrum. The strength of mixing is measured by using the squares of mixing coefficients and is considered strong if multiple configurations of the same \( J \) and parity contribute to the atomic state in near equal amounts. The calculations show that the Auger line observed at 38.42 eV in Fig. 2(b), which could be interpreted as the 4s24p\(^5\) \( 1p \) state, is better described by the 4s24p\(^4\)d (c\(_1\)) configuration. In a similar way, the Auger line observed at 26.58 eV in Fig. 2(b) is characterized by strong mixing between 4s4p\(^5\)d (b\(_2\)) and 4s\(^5\)4p\(^0\) (a) configurations. This is in contrast with Nahon et al. [21] where the line was assigned as a pure 4s\(^5\)4p\(^0\) state. The other configurations that are essential to reproduce the experimental Auger spectrum are b\(_1\): 4s4p\(^4\)(5s, 6s/7s/9d) and c\(_{2x}\): 4s\(^2\)4p\(^3\)(5s, nd).

The Auger lines in the kinetic energy range from 28 to 38 eV present a structure in Br richer than that of its Kr+ counterpart, where a peak dominates (c\(_{2y}\)) and is described by a 4s\(^2\)4p\(^3\)5d configuration. Theoretical inspection reveals that the lines in Br can be assigned to c\(_{2x}\) configurations 4s\(^2\)4p\(^3\)n\(\ell\) in which \( n\ell \) is the 5s, 5d, 6d, 7d, 8d, or 9d orbital (in the order of decreasing kinetic energy) in the dominant configuration. On the lower-energy side of c\(_{2x}\), at about 25 eV kinetic energy, two line groups, a(b\(_2\)) and b\(_1\), with clear equivalents in the Kr+ decay spectra (see Fig. 3 and Refs. [8,16]) are seen. The line group c\(_1\) in the calculated spectrum is not unambiguously identifiable from the measurement but has an equivalent in the Kr+ spectrum. Based on the simulations the lines in the case of Br feature considerable 4s\(^3\)4p\(^0\)- 4s4p\(^5\)nd mixing all the way to 4s4p\(^9\)d. The corresponding lines in Kr+ feature a much weaker mixing. The strong mixing in Br can be attributed to the lower effective nuclear charge the electrons of Br experience when compared to Kr+, which brings the 4s4p\(^5\)nd levels closer to the 4s\(^5\)4p\(^0\) level and each other, which in turn increases configuration mixing. At around 20 eV kinetic energy an increasing background with few barely distinguishable features can be seen. This kind of increasing background at low kinetic energies is inherent to magnetic bottle data and is associated with secondary electrons emitted from surfaces. Our calculations, however, predict an intense line labeled as peak a, at around 10 eV in Fig. 2(d). The peak is clearly visible in the lifted dotted line representing the calculated spectrum without including the contribution of final-state broadening to the widths. The observation can be understood by considering the double-Auger decay of the 3d\(_{3/2}\) hole, as discussed in the following subsection. The sharp
obtained by integrating along the constant excess energy in the and Rb in the right gives states formed in double-Auger decay. All levels are referenced relative to the 3d−1 levels are obtained for Br from Ref. [19], for Kr+ from Ref. [33], and for Rb2+ from the Ph.D. thesis of Khalal [18]. The other levels are from the NIST tables [34].

peaks observed below 10 eV in the measured spectra in Fig. 2 are not reproduced in the calculated spectrum, because they correspond to second-step Auger electrons leading to the formation of Br2+ and are thus not included in the simulation of the first step.

**B. Double-Auger decay of the 3d92+ hole in Br**

When comparing the double-Auger decay along the studied isoelectronic series, the first observation is that the kinetic energy of electrons involved increases with decreasing nuclear charge (up to 31 eV in Br, against 19.6 eV for Kr+ and 5.3 eV for Rb2+). The highest possible value can be deduced from the energy levels in Fig. 4 and is also indicated in Fig. 3 as striped vertical bars. Our coincidence experiments give an estimate of 38 ± 5% for the probability of the 3d92+ hole to decay by emission of two Auger electrons in Br compared to a value of 28.4 ± 1% in Kr+ [8]. This larger double-Auger probability is mainly explained by the fact that in the case of Br the intense Auger peak at 26.58 eV arising from Auger decay to the 4s24p6 state lies in the double-Auger continuum, which allows it to decay further. As explained previously, our calculation shown in Fig. 2(d) finds the 4s04p6 state to be strongly mixed with 4s4p4d state (J = 0) states. However, including the further decay of this state, shown as a solid line in Fig. 2(d), provides an overestimated width in comparison to the experimental observation.

The Br2+ states populated in the double-Auger decay of the 3d92+ hole are displayed in Fig. 1(d). This spectrum is obtained by integrating along the constant excess energy in the two-dimensional spectrum shown in Fig. 1(c), as explained in the experimental part. One observes that this double-Auger decay populates mainly the 4s24p3 (5P, 3D, 1P) and 4s4p4 (2D) Br2+ states. The intensity distribution along these lines is represented in Fig. 5 for three selected states. It gives an indication of the mechanisms of the double-Auger decay into these states. One observes peaks associated with cascade double-Auger decay and continuous intensity associated with direct double-Auger decay. This direct double-Auger path is observed as a u-shaped intensity of ~10–20 coincidence counts in Fig. 5. Interestingly this direct double-Auger decay populates the 4s24p3 (5P) and 4s4p4 (2D) Br2+ states, but not the 4s24p2 (5S) one, which is essentially populated by cascade decays. The sharp peaks below 2 eV for the formation of this 4s24p2 (5S) Br2+ ground state indicate that the cascade decays involve mainly 4s24p3 (2D) nℓ Br+ intermediate states, which converge to the 4s24p3 (2D) Br2+ state. Note the continuity in intensity between the population of the high 4s24p3 (2D) nℓ Br+ Rydberg states and that of the [4s24p3 (2D) Br2+] e− continuum. In other words, we observe a continuity between the direct double-Auger decay to the 4s24p3 (2D) Br2+ state and the cascade double-Auger decay through the associated 4s24p3 (2D) nℓ Br+ Rydberg states.

Other cascade double-Auger paths are observed in Figs. 1 and 5 and associated with Br+ intermediate states. The calculations (dotted lines) in Fig. 2(d) identify several such states of configuration a is also predicted to cause the Auger peak at 10 eV. The inclusion of its further cascade decay to the 4s4p4 (2D) Br2+ state smears out the peak to a continuum-like structure. The calculated lifetime broadening of the line turned out to be very sensitive to the selected basis set, in a way that inclusion of a certain configuration mixing expanded the width to over 100 eV, which is clearly incorrect. The most reliable value, in terms of reproducibility with a varying set of configurations, we obtained is 12 eV, which corresponds to lifetime of about 30 as, but it is probably still somewhat...
overestimated. The line is, however, an interesting demonstration of the power of very large final-state lifetime broadening to hide Auger electron lines when relying on conventional one-electron detection.

C. Comparison of the Auger decay of the 3d0 hole within the isoelectronic Br, Kr+, and Rb2+ series

The experimental magnetic bottle time-of-flight measured Auger electron spectra resulting from the decay of the 3d0, 4s24p5 state in Br, Kr+, and Rb2+ are presented as solid lines (blue) in the upper panels of their respective frames in Fig. 3. The lower panel of each frame shows the corresponding spectra (in red) simulated with FAC. The labeling scheme follows the one described for Br in Fig. 2.

The MsNN Auger decay spectra of all three atoms in the isoelectronic series resemble each other to such a degree that it is possible to visually identify the corresponding line groups in the kinetic energy range from approximately 10 to 60 eV. We observe certain trends in Fig. 3 when moving from Br to Rb2+. One such trend is the structure of the spectrum being richest in the case of Br and becoming simpler with Kr+ and Rb2+. The line group c1c2, which in Br spectrum can be found between 30 and 37 eV, lies at lower kinetic energies between 26 and 32 eV in the case of Kr+ and between 25 and 30 eV in Rb2+. According to our calculations the mixing between 4s4p5−4s24p5nd configurations, where n = 5,..., 9, decreases with increasing nuclear charge. This contribution gives the group its complex structure in the Br case. On the lower kinetic energy side of this group we see groups labeled a(b2)/b2, c1c25d (absent in Kr+) and b1 in the order of descending kinetic energy. The most intense peak in the b1 group at around 21 eV in the measured Rb2+ spectrum seems to be split in two, a feature not reproduced in our spectrum simulated with FAC. The discrepancy is discussed in the next subsection.

We can also see from Fig. 3 that except for line groups highest in kinetic energy e (4s4p5d) and d(c1) (4s4p5d), all the groups move towards lower kinetic energies as the atomic number increases within the isoelectronic series. Group e moves towards higher energy and the location of d(c1) seems to stay relatively constant. Kinetic energies of Auger electrons represent differences in total energies between the initial and various final states of the first step of the decay. A selection of such states with respect to the 4s24p5 2P0 state is presented as an energy level diagram in Fig. 4. By looking at the diagram one can get an idea of how the energy levels behave as a function of Z. From the aforementioned trends within the isoelectronic series in Fig. 3 one can see that as Z increases the states characterized by the configuration 4s24p6 (group e in Fig. 3) move further away (downwards in Fig. 4) from the the initial 3d−1 states, whereas the energy differences between the initial and the 4s24p5 states remains almost constant. The states dominated by the other configurations such as 4s24p5ns (n = 5s), and 4s24p6 (n = 5s) (labels a, b1/b2, and c1c2 in Fig. 3, respectively) move closer to the initial hole state as Z increases.

The reason for such opposite behavior of different intermediate states relative to the 3d−14s24p5 state lies in how the states are affected by an increase in the effective nuclear charge experienced by the electrons of interest when moving from Br to Rb2+. The atomic states that shift towards lower energies or stay approximately the same relative to the initial 3d−1 state as the atomic number Z increases are characterized by configurations 4s24p5 (e) and 4s4p5 (d), respectively. The states in which the leading configuration is 4s04p6 (a) or has nd5s (n = 4, ..., 9) orbital singly occupied move closer to the 3d−1 hole state in energy (upwards in Fig. 4). From this one can see that the increasing effective nuclear charge has a stronger binding effect on the energies of states of 4s24p5 and 4s4p5 configurations than on other states. The electrons in s subshells are in general more sensitive than those on other subshells to the changes in the nuclear charge. It should be noted that the general trends of the energies of the line groups can be described even in the single-configuration scheme, which rules out the influence of configuration interaction on the observed behavior.

D. Complementary information on Auger decay of the 3d0 hole in Kr+ and Rb2+

The present identifications of the peaks in the Kr+ spectrum are in agreement with studies [8,16], though it is noted that the main contributing configurations are not always identical. This discrepancy can be attributed to the atomic states in this energy region being sensitive to configuration interaction. The effect can be easily observed in Fig. 3 at around 40 eV with the d/c1 line group, which has a simple structure and can be reproduced in computations even with a single-configuration calculation including the 4s4p5 (d) configuration. In the multiconfiguration scheme, 4s4p5, however, is not the leading configuration for all the lines in the group throughout the isoelectronic series as it readily mixes with the 4s524p34d configuration. The overall shape and the intensity distribution are, however, similar between single-configuration and multiconfiguration calculations.

The seemingly split peak in the Rb2+ Auger spectrum at about 21 eV kinetic energy in the measured spectrum in Fig. 3 is not reproduced by the FAC calculations. To study this feature and investigate the sensitivity of calculations to the selected atomic code, Fig. 6 provides comparison between Rb2+ MsNN Auger spectra obtained using GRASP2K and FAC. As can be seen, the GRASP2K calculation presented in the middle panel of Fig. 6 reproduces the double-peak structure at about 24 eV kinetic energy. According to the analysis based on the GRASP2K calculation the structure is not a split peak, but instead two lines originating from decays into states of opposite parity. Based on the FAC calculation, the line at lower kinetic energy has been identified to belong to the 4s4p54d (b1) group earlier in this section. The line can be found throughout the isoelectronic series as can be seen in Fig. 3. The GRASP2K simulation, however, suggests that the leading configuration of the state is 4s04p6 (a) with 4s4p54d (b2) as the second-largest contributor. This difference between the two calculations further demonstrates the sensitivity of simulations of these atomic states to the effects of configuration interaction and small numerical differences.

The peak on the higher kinetic energy side seems to be absent in the FAC simulation, but based on calculations with GRASP2K, can be assigned to the 4s24p54d (c1) group. This
are explained in the legend of Fig. 2. Experimental intensities are the measured count numbers divided by using GRASP2K (brown) and FAC (red) presented in kinetic energy. FAC yields better results.

makes the peak a part of the line group stretching from 24 to 29 eV and defined by c1/c2 in the middle panel of Fig. 6; thus in the FAC calculation the corresponding line is c2 at 25 eV. This interpretation means that these two lines happen to lie at almost the same energy, appearing as something which at a glance looks like a split peak. The smaller configuration space used in the GRASP2K calculations seems to be able to reproduce the decay spectrum in the case of Rb2+ better than FAC. On the other hand, for Br and Kr+, the large set used in FAC yields better results.

V. CONCLUSIONS

The Auger decay following the 3d3/2-hole state in the electron configuration 3d−14s2−p6 was studied using synchrotron radiation and recorded with a magnetic bottle time-of-flight setup for the isoelectronic series of Br, Kr+, and Rb3+. The 3d5/2-hole decay spectrum in Br was also recorded with a high-resolution hemispherical energy analyzer. Interpretation of the results was done with the aid of MCD calculations and, in contrast with earlier studies, complemented by the study of the evolution of experimental and theoretical line energies along the isoelectronic series. A good agreement, albeit with some differences in the predicted intensities, between the measurements and theoretical predictions was reached, which enabled us to identify the lines visible in the Br Auger decay spectrum and interpret the corresponding coincidence map as well as discover trends in the spectral features within the studied isoelectronic series.

The 3d5/2 double-Auger decay is found to be more probable in Br than in the other systems, based on energy considerations from Fig. 4 and on our coincidence measurements. An increased contribution of electron configurations, in which the nd (n = 4, . . . , 9) subshell is singly occupied, was observed in Br. The strength of the configuration interaction was found to be inversely proportional to the atomic number Z within the isoelectronic series. This and the observed evolution of the energies of different corresponding states within the series are attributed to the increased effective nuclear charge experienced by the electrons of interest as Z increases.

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