

Double and triple photoionization of the Be-like B^+ ion: Role of double- K -shell-vacancy states

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Double and triple photoionization of Be-like B^+ ions have been studied in the photon-energy range from approximately 250 to 1300 eV. The method of merged photon and ion beams was employed and calculations were performed in support of the experiments making use of different theoretical approaches. The cross section σ_{13} for net double ionization in the investigated photon-energy range is dominated by direct removal of one K -shell electron and subsequent single-Auger decay. K -shell ionization is described very well by theory. Accordingly, measured yields of B^{3+} photoproducts were normalized to theory to obtain absolute cross sections σ_{13} . Aside from the process of direct single ionization plus autoionization, σ_{13} additionally contains contributions from photoexcited double- K -shell-vacancy B^+ resonances, from direct double L -shell ionization, and from direct double ionization involving one L -shell and one K -shell electron. We show that, apart from single K -shell ionization with subsequent Auger decay, all these processes are of minor importance for σ_{13} . Nevertheless, the sensitivity of our experiment allowed us to observe the $2s^2 2p 3s \ ^1P_1$ double- K -shell-vacancy resonance and to determine its energy, width, strength, and asymmetry parameter. Relativistic Hartree-Fock theory was employed to characterize the role of such resonances in σ_{13} . The cross section σ_{14} for net triple ionization of B^+ is expected to arise primarily from direct double K -shell ionization and subsequent single-Auger decay. The experimental cross section is found to be larger than theoretical predictions. Possible additional contributions to σ_{14} such as K -shell ionization with accompanying K -shell excitation and subsequent Auger decay are discussed, as is the influence of metastable ions in the primary B^+ ion beam.

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I. INTRODUCTION

Within a joint experimental and theoretical project, we are studying fundamental photoprocesses of few-electron boron ions in a wide photon-energy range. In particular, the present paper deals with multiple ionization of the berylliumlike B^+

ion by a single photon at energies ranging from approximately 250 eV, i.e., about 30 eV above the B^+ K edge at 217.88 eV, up to 1300 eV, far beyond the K edge. Multielectron processes and multiply excited states are addressed.

In preceding publications originating from the present project, photoexcitation of double- K -shell-vacancy states in He-like B^{3+} ions was investigated [1] and the role of such hollow ionic states in the net single photoionization of ground-state $B^{3+}(1s^2 \ ^1S)$ and metastable $B^{3+}(1s2s \ ^3S)$ ions was explored. Extremely accurate resonance parameters were calculated, with a focus on the determination of resonance energies, which were obtained with uncertainties of less than 1 meV. A follow-up paper focused on direct photo double ionization of the two-electron B^{3+} ion and also provided

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information on the single ionization of hydrogenlike B^{4+} [2]. Next in this line of experimental and theoretical efforts to understand complex photoprocesses with ions along the boron isonuclear sequence was Li-like B^{2+} , for which single and double photoionization mechanisms were studied [3].

Photoionization of boron ions was investigated previously also in low-energy experiments. Cross sections for single photoionization of B^+ were measured and calculated at photon energies between about 20 and 32 eV, where valence-shell excitations [4] are important. Core excitations of B^+ were investigated at energies from 193 to 215 eV, i.e., in the vicinity of the K edge [5]. Single photoionization of B^{2+} involving the K shell has been studied in the photon-energy range of 199–238 eV [6]. In the present project, the photon-energy range is extended considerably compared to these previous studies. It reaches up to approximately 6 times the K edge.

Here, we report on experiments elucidating higher-order processes and complex multiply-excited structures that play a role in the double and triple photoionization of Be-like ground-state $B^+(1s^2 2s^2 \ ^1S)$ and metastable $B^+(1s^2 2s 2p \ ^3P)$ ions. Employing a number of different theoretical approaches, the experimental results are dissected under the aspect of identifying the contributing reaction pathways. In particular, we were able to quantify the role of double- K -hole states in double and triple photoionization of B^+ ions. For the first time, we could demonstrate photoexcitation of an empty- K -shell (hollow) resonance in any four-electron ion, namely, the $B^+(2s^2 2p \ 3s \ ^1P_1)$ level.

This paper is organized as follows. Following this Introduction, in Sec. II the experimental procedures are outlined. Section III presents and discusses the experimental and theoretical results for double and triple ionization of B^+ by a single photon. The paper ends with a summary (Sec. IV).

II. EXPERIMENT

The experiment was conducted at the soft-x-ray beamline P04 [7] of the synchrotron lightsource PETRA III [8] operated by DESY in Hamburg, Germany. The permanent end station PIPE (photon-ion spectrometer at PETRA III) [9] of beamline P04 provided the complete experimental setup needed for the present measurements. The photon-ion merged-beams technique [10] was employed. The experimental procedures for the measurement of cross sections at PIPE have been previously described in great detail [11,12]. The present measurements were part of an experimental campaign aiming at photoionization of boron ions. First results and the techniques employed in that campaign have already been published [1–3]. Therefore, the present description of the experimental procedures is kept at a minimum.

The boron ions were produced in an electron-cyclotron-resonance ion source (ECRIS) from BF_3 gas. Typical electrical currents of the collimated B^+ ion beam in the photon-ion interaction region were 25 nA, corresponding to a low ion density of slightly less than $500\,000\text{ cm}^{-3}$. It is known that an ECRIS produces berylliumlike ions not only in their $1s^2 2s^2 \ ^1S_0$ ground level but also in the metastable $1s^2 2s 2p \ ^3P_{0,1,2}$ excited levels. Accordingly, all measurements were carried out on a mixture of ground-level and metastable ions.

Usually, the term *cross section* is applied to processes that start from a well-defined initial state and produce a well-defined final state. Since the present experiment is dealing with a mixture of ground-state and metastable excited-state ions, we introduce the term *apparent cross section* in order to distinguish the present case from the regular one. Apparent cross sections are measured in the same way as regular cross sections but depend on an additional experiment-specific parameter which, in the present context, is the fraction f of metastable B^+ ions in the parent ion beam. Consequently, we introduce the apparent experimental cross sections σ_{13}^{app} for net double and σ_{14}^{app} for net triple photoionization of B^+ .

In previous experiments employing an identical type of ECRIS, fractions of metastable components in B^+ ion beams were found to be 29% [4] and later in a different experiment 40% [5]. The metastable fraction depends on the operating conditions of the ECRIS. It could not be measured or monitored directly in our experiment, and therefore we adopted the best available estimate based on two previous measurements performed with the same type of source under closely comparable conditions. For the present work, we assumed the fraction of metastable ^3P ions to be $f = 0.35 \pm 0.06$, which is the mean of the previously found metastable contents with an uncertainty covering both of the observed fractions. This uncertainty is propagated into the systematic uncertainty of the cross sections reported in the present study.

A blazed 400-lines-per-millimeter grating with Pt coating was used to achieve the highest possible photon flux. The flux ϕ_{ph} of the transmitted photon beam was recorded by a calibrated photodiode. Overview measurements were carried out with a monochromator exit-slit width $w_{\text{es}} = 1000\text{ }\mu\text{m}$. The photon-energy region near 450 eV expected to contain the strongest hollow- K -shell resonance was scanned with $w_{\text{es}} = 400\text{ }\mu\text{m}$ at a photon flux of $\approx 5.5 \times 10^{13}$ photons per second. At a photon energy of $E_{\text{ph}} = 500\text{ eV}$, $w_{\text{es}} = 1000\text{ }\mu\text{m}$ resulted in a photon flux of $\phi_{\text{ph}} \approx 1.1 \times 10^{14}$ photons per second and $w_{\text{es}} = 400\text{ }\mu\text{m}$ gave $\approx 6.2 \times 10^{13}$ photons per second.

With $w_{\text{es}} = 1000\text{ }\mu\text{m}$ the photon beam had an energy spread of about 700 meV at $E_{\text{ph}} = 500\text{ eV}$. The photon-energy spread could be reduced to 400 meV by setting $w_{\text{es}} = 400\text{ }\mu\text{m}$. The energy axis for the present ion-yield and cross-section data is accurate within an error margin of $\pm 0.1\text{ eV}$. The Doppler shift of photon energies by approximately a factor of $1 + v_{\text{ion}}/c = 1.001\,083$ due to the counterpropagating photon and ion beams was corrected for, considering the ion velocity $v_{\text{ion}} = 3.24 \times 10^5\text{ m/s}$ and the speed of light in vacuum c .

Yields of B^{3+} and B^{4+} ions produced as a result of single-photon absorption by B^+ parent ions were recorded in energy-scan measurements covering desired energy ranges between approximately 250 and 1300 eV. The collection and detection efficiencies for the product ions are close to 100%, as described in previous publications [11,12]. The overlap factor of the photon and ion beams was not separately determined and monitored. Nevertheless, the measured yields can be put on an absolute cross-section scale by a suitable normalization function $A_{\text{corr}}(E_{\text{ph}})$.

The normalization or correction function for the present set of measurements with B^+ ions is defined as the ratio of the apparent cross sections $\sigma_{13}^{\text{app}}(E_{\text{ph}})$ for net double ionization

TABLE I. Energies in electron volts for electron rearrangement processes starting from the ground level of the B^+ ion. The numbers in parentheses denote the uncertainties of the last figures. With one exception (*), the energies were taken or inferred from the NIST Atomic Spectra Database [14] as of April 2026. The exceptional energy (*) was derived from Refs. [3] and [14].

Energy	Level reached from $1s^2 2s^2 {}^1S_0$
4.629 017(5)	$1s^2 2s 2p {}^3P_0$
4.629 775(4)	$1s^2 2s 2p {}^3P_1$
4.631 777(4)	$1s^2 2s 2p {}^3P_2$
25.154 83(5)	$1s^2 2s {}^2S_{1/2}$ (single ionization)
63.085 42(12)	$1s^2 {}^1S_0$ (double ionization)
217.88(3)	$1s 2s^2 {}^2S_{1/2}$ (K edge)
322.459 80(13)	$1s {}^2S_{1/2}$ (triple ionization)
461.2(1)*	$2s^2 2p {}^2P$ (ionization with excitation)
508.85(23)	$2s^2 {}^1S_0$ (double K -shell ionization)

of B^+ and the measured energy-dependent yields Y_3 of B^{3+} product ions generated from B^+ ,

$$A_{\text{corr}}(E_{\text{ph}}) = \sigma_{13}^{\text{app}}(E_{\text{ph}})/Y_3(E_{\text{ph}}). \quad (1)$$

Alternatively, $A_{\text{corr}}(E_{\text{ph}})$ could be obtained from the ratio $\sigma_{14}^{\text{app}}(E_{\text{ph}})/Y_4(E_{\text{ph}})$. However, there is no suitable way to get reliable numbers for $\sigma_{14}^{\text{app}}(E_{\text{ph}})$ from existing data. Since neither $\sigma_{13}^{\text{app}}(E_{\text{ph}})$ nor $\sigma_{14}^{\text{app}}(E_{\text{ph}})$ could be obtained experimentally, theory was employed. In particular, $\sigma_{13}^{\text{app}}(E_{\text{ph}})$ can be modeled relatively straightforwardly, and this has been done as accurately as possible. This modeling is briefly described below and discussed in greater detail in Sec. III A. The theory-based correction was then applied to measured yields Y_4 of B^{4+} products by multiplying them with $A_{\text{corr}}(E_{\text{ph}})$ from Eq. (1) to obtain the apparent experimental cross section $\sigma_{14}^{\text{app}}(E_{\text{ph}}) = Y_4(E_{\text{ph}})A_{\text{corr}}(E_{\text{ph}})$ for net triple ionization of a mixture of ground-state and metastable B^+ ions.

The apparent double-ionization cross section σ_{13}^{app} is closely related to the known cross-section function σ_{1s}^{dir} for direct single K -shell ionization of B^+ . It includes contributions of direct photo double ionization involving combinations of K - and L -shell electrons. Single K -shell ionization of a light atom or ion such as B^+ produces a K -shell-vacancy state that decays with almost 100% probability by an Auger process [13]. Thus, σ_{1s}^{dir} contributes to net double ionization of the B^+ ion. Our analysis shows that σ_{1s}^{dir} is by far the dominant contribution and is practically identical to the apparent double-ionization cross section σ_{13}^{app} in the energy range of our present interest. In the following Sec. III, more details of the normalization procedure and the resulting uncertainties of the experimental cross sections are explained on the basis of theoretical results.

III. RESULTS AND DISCUSSION

Single-photon-induced rearrangement of electrons in B^+ ions and mechanisms of single and multiple ionization are the main topics of this paper. For the ease of reading, we present relevant level energies and thresholds in Table I. All entries were taken from or inferred from the NIST Atomic Spectra Database [14]. For processes starting from metastable

$B^+(1s^2 2s 2p {}^3P_{0,1,2})$ ions, threshold energies are lower by up to approximately 4.6 eV as compared to the respective processes starting from the ground level.

Throughout this paper, we use the expressions single, double, or triple photoionization for describing processes characterized by their final net result, namely, the loss of one, two, or three electrons, respectively, originating from the absorption of a single photon. This can occur via direct or indirect (multistep) processes. An example for double photoionization is the two-step mechanism starting with direct (knock-off) removal of an inner-shell electron and ending with the emission of an Auger electron. In contrast to that, we use, e.g., the term photo double ionization (PDI) to describe the direct nonsequential removal of two electrons by a single photon. PDI is one of the possible mechanisms summarized under the term double photoionization.

A. Double photoionization of B^+

In the present energy range far above the K edge, outer-shell ionization is relatively insignificant and K -shell ionization prevails. The cross section σ_{2s}^{dir} for direct ionization of a $2s$ electron is approximately 2.5 Mb at the L edge [4,15] and drops from there to 0.036 Mb at 250 eV [15]. At that same energy, the cross section σ_{1s}^{dir} for direct ionization of a $1s$ electron reaches 0.835 Mb [15] and the ratio $\sigma_{1s}^{\text{dir}}/\sigma_{2s}^{\text{dir}}$ increases with increasing photon energy.

Single photoionization of the K shell with or without accompanying L -shell excitation

$$\gamma + B^+(1s^2 2s 2\ell) \rightarrow B^{2+}(1s 2\ell n\ell') + e^- \quad (\ell = 0, 1) \quad (2)$$

produces an autoionizing state that decays by an Auger process with almost 100% probability. The removal of one K -shell electron followed by the emission of an Auger electron thus contributes to net double photoionization of the B^+ ion. Principal quantum numbers in Eq. (2) are $n \geq 2$ and orbital quantum numbers ℓ' can be anywhere between 0 and $n-1$. In the experiments, removal of a single K -shell electron is essentially observed by monitoring the production of B^{3+} ions.

Several additional mechanisms producing B^{3+} from B^+ by the absorption of a single photon contribute to double ionization of B^+ . These are as follows:

(1) direct nonsequential PDI of the L shell

$$\gamma + B^+(1s^2 2s 2\ell) \rightarrow B^{3+}(1s^2) + 2e^-; \quad (3)$$

(2) PDI of one L -shell and one K -shell electron

$$\gamma + B^+(1s^2 2s 2\ell) \rightarrow B^{3+}(1s n\ell') + 2e^-, \quad (4)$$

where a nonautoionizing state is produced that can only stabilize radiatively; and

(3) photo double excitation of the K shell with subsequent emission of two electrons either sequentially or simultaneously

$$\begin{aligned} \gamma + B^+(1s^2 2s 2\ell) &\rightarrow B^+(2s 2\ell n\ell' n'\ell'') \\ &\rightarrow B^{3+}(1s^2) + 2e^-, \end{aligned} \quad (5)$$

where $n, n' \geq 2$ and $0 \leq \ell', \ell'' \leq (n-1), (n'-1)$, respectively. Triple and even quadruple excitations are also possible

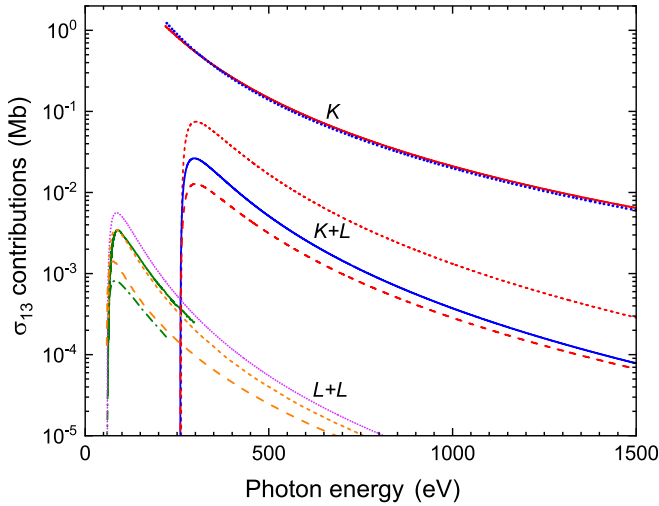


FIG. 1. Calculated contributions to the cross section σ_{13} for net double photoionization of B^+ ions. The dominant contribution is from direct single K -shell ionization which is independent of whether B^+ is in its ground state or in one of the ^3P metastable levels. It is represented by the group of curves labeled “ K .” In that group, the red solid line is the result of Verner *et al.* [15], while the blue dotted line was obtained from present RPAE calculations. In the group labeled “ $K + L$,” cross sections for the nonsequential removal of one K -shell and one L -shell electron are shown. All the associated results were obtained from the PDI model [16]. The red short-dashed and long-dashed lines are σ_{1s+2s} and σ_{1s+2p} for metastable B^+ . The blue solid line is σ_{1s+2s} for ground-state B^+ . The third group labeled “ $L + L$ ” shows cross sections for the removal of the two outer-shell electrons. The green solid line and the green chain curve are σ_{2s+2s} for ground-state and σ_{2s+2p} for metastable B^+ , respectively, from the work of McIntyre *et al.* [17,18]. The orange dashed and long-dashed lines correspond to the green lines. They were calculated using the present CCC approach. The magenta dotted line is the PDI-model result [16] for σ_{2s+2s} of ground-state B^+ .

and also lead to net double ionization in almost all cases. Such resonant contributions are restricted to narrow energy ranges and can be experimentally distinguished from the smooth “background” of the processes described by Eqs. (2)–(4). Figure 1 shows calculated cross sections of B^+ ions in the ground level and in the $1s^2 2s 2p$ ^3P excited levels for the nonresonant processes contributing to net double ionization. PDI of the L shell has the lowest threshold energy. This amounts to 63.085 eV for the ground level and is near 58.5 eV for each of the three metastable levels of B^+ [14]. Three different approaches have been used to calculate the cross sections for $L + L$ PDI, that is, the simultaneous removal of the two L -shell electrons by a single photon.

Previously, McIntyre *et al.* have carried out calculations of PDI of berylliumlike systems using the intermediate energy R -matrix (IERM) method [19]. Results were obtained for both ground-level [17] and excited Be-like systems [18]. While data for ground-level B^+ can be directly taken from the published paper [17], cross sections for metastable B^+ have to be inferred from the scaling proposed in Ref. [18]. The results obtained by McIntyre *et al.* are shown in Fig. 1 within the group of cross sections labeled $L + L$. Calculations of these same cross sections have been carried out using the convergent

close coupling (CCC) theory. The results for $2s + 2s$ and $2s + 2p$ PDI are a part of the $L + L$ group of cross sections in Fig. 1.

The CCC approach to photoionization problems has been described in great detail previously [20–26]. It was also used and discussed within the boron photoionization project [1–3]. Recently, an overview of the method was provided in a paper dealing with single and double photoionization of the Li atom [27]. The present treatment of $(L + L)$ PDI of the B^+ ion in its ground and ^3P metastable levels makes use of an initial multiconfiguration Hartree-Fock (MCHF) state and a final state which is obtained from a CCC calculation of electron scattering on the Li-like B^{2+} ion. The latter begins with a self-consistent Hartree-Fock calculation for the ground state to determine the core $1s$ orbitals. These define the frozen-core Hartree-Fock potential, which is used in the diagonalization of the B^{2+} Hamiltonian in a truncated Laguerre basis to obtain a discretization of the true B^{2+} one-electron target spectrum. The basic premise of the CCC method is that as the basis size is increased, the results converge to the true solution of the problem. Presently, to obtain convergent results, we take the maximum orbital angular momentum $\ell_{\max} = 4$, the exponential fall-off parameter $\lambda_\ell = 2$, and the basis size to be $N_\ell = 30 - \ell$. The two initial states of interest here per Eq. (3) are obtained by employing the multiconfiguration Dirac-Hartree-Fock (MCDHF) basis generated using the GRASP computer code [28]. The MCDHF expansion for the ground state contains 13 configurations comprising $n\ell^2$ orbitals with $n \leq 5$ and $\ell \leq 3$. The metastable excited state is represented employing 11 configurations.

The present CCC results for σ_{2s+2s} and σ_{2s+2p} are close to the cross sections obtained by McIntyre *et al.* [17,18]. A third calculation of the $L + L$ PDI cross section shown in Fig. 1 is based on the PDI model developed by Kheifets [16]. This model has been successfully used for a number of applications [3,16,27,29,30] and appears to reproduce measured $K + L$ PDI cross sections particularly well. The comparison with the *ab initio* $2s + 2s$ PDI calculations employing the IERM and CCC approaches is also satisfactory. This provides confidence in the $K + L$ cross sections shown in the group of curves labeled $K + L$ in Fig. 1, all of which were calculated using the PDI model.

In the third group of curves labeled K , cross sections for direct K -shell ionization are shown. The results obtained by Verner *et al.* [15] and by the present calculations using the random-phase approximation with exchange (RPAE) [31,32] are in excellent agreement with one another. Calculations using the COWAN code [33] result in a K -shell ionization cross section that is only about 3% below the other two calculations. The cross section for direct K -shell ionization of B^+ calculated by Reilman and Manson [34] also perfectly matches the other theoretical findings. This provides further evidence for the previous findings [1–3] that cross sections for direct single K -shell ionization are well known and can be calculated with good accuracy by different theoretical approaches, at least in the case of light atoms and ions with only a few electrons. In the present context, we use the result of Verner *et al.* for the modeling of the continuous part of σ_{13} . We emphasize that the RPAE and Cowan calculations for direct single K -shell

ionization for the ground-level and metastable B^+ ions are practically identical.

Figure 1 shows that contributions to σ_{13} other than direct K -shell ionization are very small. Clearly, $L + L$ contributions to σ_{13} can be neglected. Hence, a suitable model for the experimentally observed nonresonant apparent cross section σ_{13}^{app} for double ionization of B^+ can be formulated as

$$\sigma_{13}^{\text{model}} = \sigma_{1s}^{\text{dir}} + 0.35(\sigma_{1s+2s}^{\text{ms}} + \sigma_{1s+2p}^{\text{ms}}) + 0.65\sigma_{1s+2s}^{\text{gs}}, \quad (6)$$

where $\sigma_{1s+2s}^{\text{ms}}$, $\sigma_{1s+2p}^{\text{ms}}$, and $\sigma_{1s+2s}^{\text{gs}}$ are the $K + L$ PDI cross sections of metastable and ground-state B^+ , respectively. The model cross section differs from direct K -shell ionization by less than 10%, where the difference is photon-energy dependent and reaches its maximum near 340 eV. This difference is within the estimated uncertainty of the calculated nonresonant K -shell ionization cross section σ_{1s}^{dir} . The model cross section thus obtained from theory can be expected to provide a fairly accurate representation of the experimental apparent cross section σ_{13}^{app} at energies where resonances do not play a role.

The correction factor $A_{\text{corr}}(E_{\text{ph}})$ defined by Eq. (1) can now be approximated by replacing σ_{13}^{app} in Eq. (1) with $\sigma_{13}^{\text{model}}$ and using the theoretical data from Fig. 1. Due to low signal rates, the yields Y_3 of B^{3+} product ions exhibit significant scatter at high photon energies, and consequently, so do the ratios $\sigma_{13}^{\text{model}}/Y_3$. In contrast, the resulting $A_{\text{corr}}(E_{\text{ph}})$ outside resonance contributions, representing the slowly varying photon-ion beam overlap factor together with the absolute normalization, must be a smooth function of energy. In the present case, it is obtained by a polynomial fit to the ratios $\sigma_{13}^{\text{model}}/Y_3$. The purpose of establishing $A_{\text{corr}}(E_{\text{ph}})$ is twofold. With $A_{\text{corr}}(E_{\text{ph}})$ known, fine measurements of Y_3 in the vicinity of resonances as well as measured yields Y_4 can be put on an absolute cross-section scale. As a result, resonance contributions to σ_{13}^{app} can be fully quantified without additional input from theory, and absolute cross sections σ_{14}^{app} can be determined within the given uncertainty range.

The apparent cross section σ_{13}^{app} resulting from the normalization of Y_3 to $\sigma_{13}^{\text{model}}$ is represented in Fig. 2 by open circles with statistical error bars. On the scale of the figure, the model cross section (red solid line) can barely be distinguished from that of direct K -shell ionization (blue dashed line). Of course, the experimental apparent cross sections σ_{13}^{app} , within their statistical uncertainties, agree with $\sigma_{13}^{\text{model}}$, to which they have been normalized. The conservatively estimated total-uncertainty range of σ_{13}^{app} is within the gray solid lines in Fig. 2. The upper and lower limits of σ_{13}^{app} consider the following uncertainties:

- (1) a possible 10% error in the calculation of σ_{1s}^{dir} and
- (2) a possible factor of 2 error in the calculation of cross sections from the PDI model.

The experimental cross section σ_{13}^{app} appears to be smooth given the limited energy resolution at exit-slit width $w_{\text{es}} = 1000 \mu\text{m}$ and the relatively coarse step size of the energy scan data shown in Fig. 2. In the investigated photon-energy range, K -shell double-excitation resonances [see Eq. (5)] have to be expected. An experimental demonstration of one such resonance has been provided previously by Hasegawa *et al.* for the neutral Be atom [35], and this remained the only successful

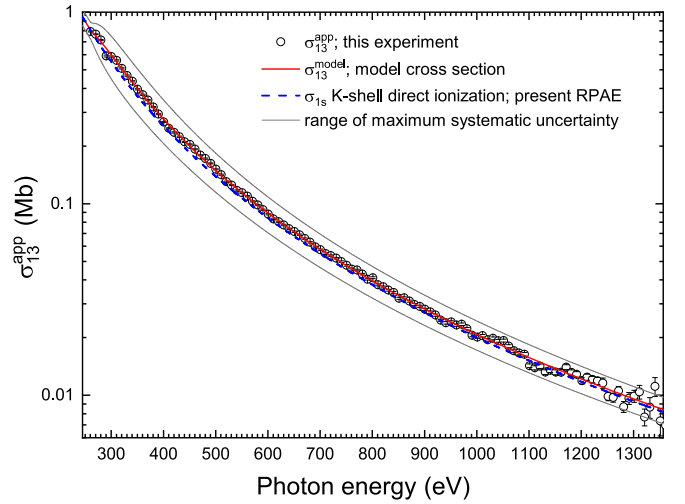


FIG. 2. Theoretical and experiment-based apparent cross sections σ_{13}^{app} for net double photoionization of the B^+ ion. The present normalized yield data are represented by open circles together with their statistical error bars. The red solid line is the theory-based model cross section $\sigma_{13}^{\text{model}}$. The blue dashed line represents the present RPAE result for σ_{1s}^{dir} . The gray solid lines indicate the maximum uncertainty (upper and lower limits) of σ_{13}^{app} .

attempt to observe double- K -hole “quadruply excited” states in any berylliumlike system so far.

For a better understanding of the role of double-core-hole resonances in the photoionization of B^+ ions, photoabsorption cross sections for the $^1S_0$, $^3P_0$, $^3P_1$, and $^3P_2$ initial states were derived from *ab initio* configuration-interaction (CI) calculations on the basis of the Hartree-Fock method with relativistic extensions (HFR) applying the COWAN code [33]. The theoretical approach has been described in detail previously [36].

A direct one-electron dipole excitation from the $B^+ 1s^2 2s^2$ ground-state configuration to double-core-hole configurations $1s^{-2}$ is not possible, since only single-electron dipole matrix elements are considered in the present HFR approach. This limitation is not related to the intensity of the radiation field, which is low in the present experiments. Hence, in the present HFR treatment, the resonant excitation from the ground state to the various B^+ double-core-hole configurations is only possible through configuration mixing via CI in the initial and excited-state configurations. For the representation of the initial and final states, the associated configuration spaces were chosen in a first step to include all configurations with principal quantum numbers up to $n = 3$ and orbital quantum numbers up to $\ell = 2$. The desired photoionization cross sections were calculated from the dipole matrix elements $M = \langle \Psi_{\epsilon\ell} | er | \Psi_i \rangle$ with the wave functions Ψ_i for the four initial levels. The wave function $\Psi_{\epsilon\ell}$ represents the residual B^{2+} ion and the ejected electron with kinetic energy ϵ and angular momentum $\ell = 0, 1, 2$.

In subsequent steps, the configuration space was expanded by adding configurations with $n = 4$ and $\ell \leq 2$ until convergence of the calculated resonance positions of the $2s^2 2p 3s$ states was obtained, i.e., the resonance energy did not change anymore when more configurations were added. The final sets of configurations employed in the present calculations

TABLE II. Configurations employed in the HFR calculations to represent the B^+ ground state. Three groups of configurations are characterized by the three possible core configurations $1s^2$, $1s^{-1}$, and $1s^{-2}$. The entries in the columns below these core configurations are the configurations of the outer-shell electrons.

$1s^2$	$1s^{-1}$	$1s^{-2}$	
$2s^2$	$2s^2 3s$	$2s^2 3s^2$	$2s 3s 3d 4d$
$2p^2$	$2s 3s^2$	$2s^2 2p^2$	$2s 3d^2 4d$
$3s^2$	$2s^2 3d$	$2s^2 2p 3p$	$2p^4$
$4s^2$	$2s 3d^2$	$2s^2 2p 4p$	$2p^3 3p$
$3p^2$	$3d^3$	$2s^2 3p 4p$	$2p^2 3p^2$
$4p^2$	$3s^2 3d$	$2s^2 3p^2$	$2p^2 4p^2$
$3d^2$	$3s 3d^2$	$2s^2 4p^2$	$2p^2 3p 4p$
$3d 4d$	$2s^2 4d$	$2s^2 3d^2$	$2p^3 4p$
$2s 3s$	$2s 3d 4d$	$2s 3s 3d^2$	$2p^2 3d^2$
$2s 3d$	$3d^2 4d$	$2s 3d^3$	$2p^2 3d 4d$
$2s 4d$	$3s^2 4d$	$2s^2 3d 4d$	
$2s 4s$	$3s 3d 4d$		
$2p 3p$	$2s^2 4s$		
$2p 4p$	$2p^2 3s$		
$3p 4p$			

to represent the ground state and the excited states are provided in Tables II and III, respectively. The natural widths Γ of the resonances were determined by calculating the Auger decay rates to the final B^{2+} electron configurations shown in Table IV.

Employing the HFR approach described above, photoabsorption cross sections for ground-level $B^+(1s^2 2s^2 {}^1S_0)$ and metastable $B^+(1s^2 2s 2p {}^3P_{0,1,2})$ ions were calculated. For the three fine-structure levels of the metastable ${}^3P$ ions with total angular momentum quantum numbers $J = 0$, $J = 1$, and $J = 2$, almost identical cross sections were found. Re-

TABLE III. Excited-state configurations of B^+ employed in the HFR calculations.

$1s^2$	$1s^{-1}$	$1s^{-2}$	
$2s 2p$	$2s^2 2p$	$2s^2 2p 3s$	$2p 3d^3$
$2s 3p$	$2s^2 3p$	$2s^2 2p 3s^2$	$3s 2p^3$
$2s 4p$	$2s^2 4p$	$2s^2 2p 4s$	$3p 3d^3$
$3s 2p$	$2s 3s 2p$	$2s^2 2p 4s^2$	$4p 3d^3$
$3s 3p$	$2s 3s 3p$	$2s^2 3s 3p$	$2s 2p 3d 4d$
$3s 4p$	$2s 3s 4p$	$2s^2 3s 4p$	$2s 3p 3d 4d$
$2p 3d$	$3s^2 2p$	$2s^2 4s 3p$	$2s 4p 3d 4d$
$3p 3d$	$3s^2 3p$	$2s^2 4s 4p$	$2p 3d^2 4d$
$4p 3d$	$3s^2 4p$	$2s 2p^3$	$3p 3d^2 4d$
$2p 4d$	$2p^3$	$2s 2p^2 3p$	$4p 3d^2 4d$
$3p 4d$	$2p^2 3p$	$2s 2p^2 4p$	$3s^2 3p 3d$
$4p 4d$	$2p^2 4p$	$2s^2 2p 3d$	$3s^2 3p 4d$
	$2p 3p 4p$	$2s^2 3p 3d$	$3s^2 4p 3d$
	$2s 2p 3d$	$2s^2 4p 3d$	$3s^2 4p 4d$
	$2p 3d^2$	$2s^2 2p 4d$	$3s^2 4s 4p$
	$2s 2p 4d$	$2s^2 3p 4d$	$3s 2p 3d^2$
	$2p 3d 4d$	$2s^2 4p 4d$	$3s 3p 3d^2$
		$2s 2p 3d^2$	$2p 3s 3d 4s$
		$2s 3p 3d^2$	$3s 3p 3d 4s$
		$2s 4p 3d^2$	

TABLE IV. Final ionic-state configurations of B^{2+} employed in the HFR calculations.

odd		even	
$1s^2 2p$	$1s 2p 3d$	$1s^2 2s$	$1s 2p 3p$
$1s^2 3p$	$1s 3p 3d$	$1s^2 3s$	$1s 2p 4p$
$1s^2 4p$	$2s^2 3p$	$1s^2 4s$	$1s 2s 3d$
$1s 2s 2p$	$2s 3s 3p$	$1s 2s^2$	$1s 3s 3d$
$1s 2s 3p$	$1s 2p 4d$	$1s 2s 3s$	$1s 3d^2$
$1s 2s 4p$	$1s 3p 4d$	$1s 2s 4s$	$1s 2s 4d$
$1s 3s 2p$		$1s 3s^2$	$1s 3s 4d$
$1s 3s 3p$		$1s 3s 4s$	$1s 3d 4d$
$1s 3s 4p$		$1s 2p^2$	$2s^2 3s$
$1s 4s 2p$		$1s 3p^2$	$2s^2 4s$
$1s 4s 3p$		$1s 4p^2$	$2s^2 3d$
$1s 4s 4p$			$2s^2 4d$

sults of the HFR calculations are shown in Fig. 3. Since the CI expansions had to be limited in size to keep the overall calculations manageable, the theoretical results are expected to be reliable at photon energies no larger than approximately 460 eV. Figure 3(a) shows the absorption cross section $\sigma_{\text{abs}}^{\text{gs}}$ for ground-state B^+ , including the lowest-energy double- K -hole resonances reachable from the ${}^1S_0$ ground level of B^+ . The resonances are labeled by capital letters, and the assignments are given in Table V together with the resonance energy E_{res} , the dipole matrix element M , and the natural width Γ .

Figure 3(b) presents the photoabsorption cross section $\sigma_{\text{abs}}^{\text{ms}}$ for metastable $B^+({}^3P_1)$ including the lowest-energy

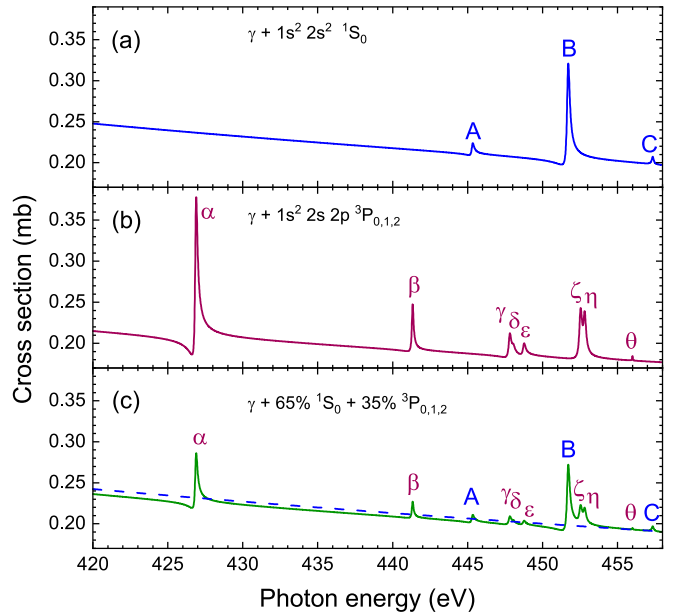


FIG. 3. Photoabsorption cross sections σ_{abs} of B^+ ions calculated by applying HFR theory. (a) $\sigma_{\text{abs}}^{\text{gs}}$ of ground-level $B^+(1s^2 2s^2 {}^1S_0)$; (b) $\sigma_{\text{abs}}^{\text{ms}}$ of metastable $B^+(1s^2 2s 2p {}^3P_{0,1,2})$; (c) $0.65\sigma_{\text{abs}}^{\text{gs}} + 0.35\sigma_{\text{abs}}^{\text{ms}}$. The blue dashed line in (c) is the model cross section constructed to represent the smooth direct-ionization contribution to the apparent cross section σ_{13}^{app} .

TABLE V. Assignments and resonance parameters of the peaks in Fig. 3 labeled by capital and Greek letters, respectively. The assigned quadruply excited levels are given in the second column and initial and final total angular momentum quantum numbers in the third and fourth column, respectively. The calculated parameters are (1) the resonance energy E_{res} above the initial state of the B^+ parent ion, (2) the associated dipole matrix element M , and (3) the natural width Γ of the resonance.

	Assigned level	J_i	J_f	E_{res} (eV)	M (a.u.)	Γ (eV)
A	$2s\ 2p^3\ ^1P$	0	1	445.310	-0.001 78	0.186
B	$2s^2\ 2p\ 3s\ ^1P$	0	1	451.688	-0.005 75	0.218
C	$2s^2\ 2p\ 3d\ ^1P$	0	1	457.347	0.001 36	0.158
α	$2s^2\ 2p^2\ ^3P$	1	0	426.854	0.006 54	0.182
		1	1	426.860	0.005 66	0.180
		1	2	426.870	-0.007 31	0.182
		1	0	441.327	0.003 17	0.145
β	$2p^4\ ^3P$	1	1	441.322	0.002 75	0.111
		1	2	441.313	-0.003 55	0.145
		1	1	447.792	-0.002 36	0.207
γ	$2s^2\ 2p\ 3p\ ^3D$	1	2	447.798	-0.004 11	0.207
		1	1	448.042	0.002 38	0.206
δ	$2s^2\ 2p\ 3p\ ^3S$	1	0	448.739	0.001 92	0.207
		1	1	448.743	0.001 65	0.206
		1	2	448.749	-0.002 12	0.205
		1	1	452.519	-0.003 07	0.205
ζ	$2s^2\ 2p\ 4p\ ^3D$	1	2	452.524	-0.005 62	0.205
		1	1	452.590	0.002 63	0.198
		1	0	452.796	0.003 56	0.206
η	$2s^2\ 2p\ 4p\ ^3P$	1	1	452.800	0.003 04	0.201
		1	2	452.806	-0.003 88	0.206
		1	1	455.997	-0.000 56	0.044
		1	2	455.997	-0.000 48	0.038
θ	$2p^3\ 3p\ ^3P$	1	1	455.997	-0.000 48	0.038
		1	2	455.997	0.000 63	0.044

double- K -hole resonances that can be reached from the ^3P term of B^+ . The calculated cross sections for the $\text{B}^+(^3P_1)$ ion are an excellent representation also for $\text{B}^+(^3P_0)$ and $\text{B}^+(^3P_2)$. Accordingly, only the data for $\text{B}^+(^3P_1)$ ions are provided in Table V. Individual double-core-hole resonances populated from metastable initial levels are labeled by Greek letters.

In Fig. 3(c), the apparent photoabsorption cross section for a mixture of 65% ground-state and 35% metastable B^+ ions is shown. In the present energy range, photoabsorption is expected to be strongly dominated by single photoionization processes (see discussion above). Hence, the results displayed in Fig. 3(c) should be directly comparable to the measured cross section σ_{13}^{app} . Accordingly, the smooth background cross section is almost identical with the model cross section $\sigma_{13}^{\text{model}}$ [see Eq. (6)], which is shown by the blue dashed line in Fig. 3(c). Indeed, the largest difference between the two background data sets is only 2.5% at 420 eV.

Within the present investigation, additional measurements of double photoionization of B^+ ions were performed with much reduced step size and better energy resolution of 400 meV in the region of expected double K -shell excitation resonances. The attempts were successful and resulted in the clear observation of such a resonance near 451-eV photon energy. At that energy, we expected the excitation

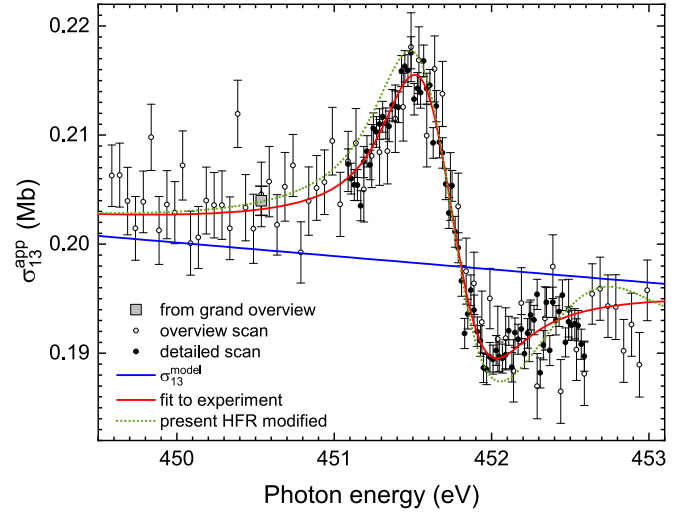


FIG. 4. Cross sections σ_{13}^{app} for double photoionization of B^+ ions. The open circles result from an overview scan of the resonance which is assigned to the quadruply excited $\text{B}^+(2s^2\ 2p\ 3s\ ^1P_1)$ populated from the ground level of B^+ . The full circles were taken at a smaller step size but with the identical resolution of 400 meV. The gray-shaded square belongs to the scan results displayed in Fig. 2. All error bars shown along with the experimental cross sections are statistical only. The blue solid line is the cross section $\sigma_{13}^{\text{model}}$ [Eq. (6)]. The red solid line is a fit to the data employing a Gaussian-convoluted Fano profile [37,38]. The green dotted line is derived from the present HFR calculations.

$\text{B}^+(1s^2\ 2s^2\ ^1S_0) \rightarrow \text{B}^+(2s^2\ 2p\ 3s\ ^1P_1)$, i.e., population of the lowest-energy dipole-allowed double- K -hole state reachable from the ground level.

The yields obtained from the scan measurements were normalized by multiplication with the correction function $A_{\text{corr}}(E_{\text{ph}})$ [see Eq. (1)]. Resulting cross sections are displayed in Fig. 4. The open circles show an overview scan and the full circles are from a detailed scan with smaller step size, both at 400-meV resolution. The gray-shaded square is one of the data points of the grand overview of σ_{13}^{app} shown in Fig. 2. The blue solid line is the model cross section $\sigma_{13}^{\text{model}}$ discussed above [see Eq. (6)].

A fit of the resulting cross sections with a Gaussian-convoluted Fano profile [37,38] produced the red solid fit curve. The fit parameters thus obtained are shown in Table VI and compared to the parameters found previously for the Be atom [35]. The uncertainties provided by the numbers in parentheses are statistical only in both the present B^+ and the previous Be measurements. We point out that the energy calibration of the present experiment is within 0.1 eV and the total uncertainty of the resonance strength is of the order of 25%. The observed resonance strength in Table VI has been normalized by a factor of 1/0.65 to account for the admixture of only 65% ground-state B^+ ions in the parent ion beam employed in this experiment.

Figure 4 also shows a green dotted line which was derived by modifying the present HFR result for the $2s^2\ 2p\ 3s\ ^1P_1$ resonance (see Table V). The asymmetry parameter $q_{\text{abs}} = 4.06$ for the calculated photoabsorption cross section does not agree with $q_{\text{ion}} = -1.51$ found in the present ionization

TABLE VI. Resonance parameters of the $2s^2 2p 3s \ ^1P_1$ double- K -hole resonance observed in double photoionization of the B^+ ion (this work) and the neutral Be atom [35]. The parameters are (1) the resonance energy E_{res} above the $1s^2 2s^2 \ ^1S_0$ ground level, (2) the Fano asymmetry parameter q_{ion} , (3) the natural width Γ of the resonance, and (4) the resonance strength S_{ion} . The numbers in parentheses behind the entries are the standard deviations of the resonance fits and correspond to the last digit(s) of the parameters obtained from the fits.

	E_{res} (eV)	q_{ion}	Γ (eV)	S_{ion} (kb eV)
B^+	451.697(12)	$-1.51(9)$	0.12(2)	7.2(1.1)
Be	275.32(2)	$-1.27(21)$	0.50(4)	—

experiment. Most evident is the opposite sign of the two Fano parameters. Also, the resonance strengths $S_{\text{abs}} = 24.5$ kb eV and $S_{\text{ion}} = 7.2$ kb eV are quite different. Part of the reason for the differences is the fact that two different cross sections are discussed here: The experimental apparent cross section σ_{13}^{app} for double photoionization is a part of the calculated total photoabsorption cross section. The green dotted curve was therefore modified relative to the calculated shape. An asymmetry parameter $q = -1.51$ was chosen instead of the calculated $q = 4.06$. The resonance strength was reduced by a factor of 0.65×0.43 and the resulting cross section was shifted up by 0.0017 Mb, i.e., by only 0.23%. The resonance energy and width were left the same as calculated. The experiment might indicate a contribution arising from the resonance pair ζ and η but is inconclusive due to the large statistical scatter of the data.

Theory and experiment agree in the resonance energy within a difference of only 11 meV. This agreement is likely fortuitous. The experimental energy scale is estimated to have a 100-meV uncertainty, and the theoretical calculations are expected to have an uncertainty of that same magnitude. Nevertheless, the level of agreement of theory and experiment provides confidence in the correct assignment of the observed resonance in the double photoionization of the B^+ ion.

Comparison of the resonance parameters listed in Table VI for the excitation of the $2s^2 2p 3s \ ^1P_1$ double- K -hole level in the B^+ ion and the neutral Be atom shows that the resonance energies scale approximately with $(Z - 0.43)^2$, where Z is the atomic number. The Fano asymmetry parameters of both measurements are the same within the experimental uncertainties. The natural width found for the resonance in B^+ is only approximately one-fourth of that in Be. This is surprising since the atomic numbers of Be and B^+ are not that different. The strength S_{ion} of the $\text{Be}(2s^2 2p 3s \ ^1P_1)$ resonance could not be determined since the experiment of Hasegawa *et al.* [35] did not provide cross sections on an absolute scale. Further experiments on hollow- K -shell resonances along the series of berylliumlike ions are necessary to clarify the situation.

B. Triple photoionization of B^+

Direct nonsequential photo triple ionization (PTI)

$$\gamma + B^+(1s^2 2s 2\ell) \rightarrow B^{4+}(1s) + 3e^- \quad (\ell = 0, 1) \quad (7)$$

in which both L -shell electrons and one K -shell electron are removed in a nonsequential interaction is expected to be extremely unlikely. A photon interacts directly with only a single atomic electron. The removal of two additional electrons requires correlated three-electron dynamics and the probability of emitting the additional electrons is very small. Nevertheless, PTI has been demonstrated previously by Wehlitz *et al.* [39] for the Li atom. The maximum cross section observed in that case was found to be roughly 5 b. PTI cross sections have to be expected to decrease very rapidly with increasing atomic number Z along an isoelectronic sequence. Part of the Z dependence is associated with the PTI threshold energy. It takes 203.49 eV to remove all three electrons from Li while the threshold energies for removing three electrons from ground-level and $2s2p \ ^3P$ metastable B^+ are 322.46 and 317.83 eV, respectively [14]. Although the berylliumlike B^+ ion provides one more electron than Li, the PTI cross section for B^+ must be much smaller than that of Li and is therefore out of reach for the present type of experiments.

Apart from the PTI mechanism, multistep processes may contribute to net triple photoionization of B^+ . Ionization of a single K -shell electron is insufficient because only one additional electron can be removed in a subsequent Auger process (there are only two valence electrons present). Excitation of a single K -shell electron transfers even less energy to the system and, therefore, can at most lead to net double ionization. Indirect triple photoionization processes must involve the creation of a double- K -hole state.

An important goal of the present experiment was the investigation of K -shell PDI

$$\gamma + B^+(1s^2 2s 2\ell) \rightarrow B^{3+}(2s 2\ell) + 2e^- \quad (8)$$

with $\ell = 0$ for ground-state B^+ and $\ell = 1$ for metastable B^+ . The resulting B^{3+} ion with two electrons above an empty K shell almost exclusively decays by the emission of an Auger electron so that a hydrogenlike $B^{4+}(1s)$ ion is finally produced.

Double K -shell ionization thresholds for ground-level and metastable B^+ are 508.85 and 505.30 eV [14] (see Table I). When rearrangement processes in the L shell are included, the lowest threshold for double K -shell ionization of the metastable B^+ leading to $B^{3+}(2s^2)$ is even lower and amounts to 504.22 eV. The process described by Eq. (8) requires a two-electron interaction. A conceivable three-electron interaction comprises processes in which the direct removal of both K -shell electrons is accompanied by additional L -shell excitation. Numerous excited states may be involved and, accordingly, a wealth of doubly excited B^{3+} levels is associated with double K -shell ionization plus single L -shell excitation of berylliumlike B^+ with threshold energies beyond 505.30 eV. However, the cross sections for such three-electron processes (including PTI) have to be expected to be very small.

Another two-electron process contributing to net triple ionization of B^+ has to be considered. From previous work on Li-like systems [3,27] it is known that processes of single K -shell ionization accompanied by K -shell excitation have small but observable cross sections. Ionization excitation (IE)

can be described as

$$\gamma + B^+(1s^2 2s 2\ell) \rightarrow B^{2+}(2s 2\ell n\ell') + e^- \quad (9)$$

with $n \geq 2$ and $0 \leq \ell' \leq (n-1)$. The intermediate B^{2+} states with two K -shell vacancies can decay by the emission of two electrons in a double-Auger process. The combination of a two-electron process in the first step and a three-electron Auger decay in the second results in small cross sections again. The lowest threshold of any such process starting from ground-level B^+ ions is 461.2(1) eV, which is inferred from the ionization energy of ≈ 25.15 eV [14] and the measured excitation energy 436.05(10) eV of the transition $B^{2+}(1s^2 2s) \rightarrow B^{2+}(2s^2 2p)$ [3]. The threshold of this possible contribution to net triple ionization of B^+ is below that of double K -shell PDI.

Finally, even resonant contributions to net triple photoionization of B^+ are possible, but are expected to have very small cross sections as well. The first step of the process is the same as the one described by Eq. (5). Depending on the degree of excitation, the resulting B^+ ion with its empty K shell can decay via different pathways, all finally leading to a B^{4+} product ion. Even the energetically lowest resonant state falling into this category, the $2s^2 2p 3s \ ^1P_1$ level, may contribute to net triple ionization via a triple-Auger decay [40]. This pathway is energetically possible because the resonance energy of about 451.7 eV is much larger than the triple-ionization threshold 322.460 eV of ground-level B^+ . More highly excited resonant states may decay by Auger cascades, implying single- and double-Auger processes, the combination of which produces the final charge state B^{4+} . Excitation of B^+ to such highly excited levels is associated with smaller cross sections, however, the probability for the emission of all in all three electrons increases with the total excitation energy due to the possibility of sequential Auger decays.

Starting from the result displayed in Fig. 4, the $2s^2 2p 3s \ ^1P_1$ resonance causes an excursion of approximately 20 kb on top of a smooth ≈ 200 -kb background of the cross section σ_{13}^{app} . The branching ratio of triple-Auger decay can be estimated to be of the order of 10^{-4} [40]. Hence, one might expect cross sections of the order of 2 b on the resonance peak. Under the conditions of the present experiment, this was not reachable. Thus, as a bottom line, it can be stated that direct double K -shell photoionization with subsequent Auger decay is the dominant contribution to σ_{14} by far.

Energy scans of triple photoionization of B^+ were performed in the experiment. The measured yields Y_4 of B^{4+} product ions were normalized by applying the correction function $A_{\text{corr}}(E_{\text{ph}})$ [see Eq. (1)]. The resulting cross sections are shown in Fig. 5. Two scan results are displayed. The yellow-shaded circles were obtained in an overview scan covering energies between about 500 and 1300 eV. The green-shaded circles were measured in a threshold scan with much reduced step size between energy points. For both data sets the statistical and the total error bars are shown. Toward higher photon energies the available photon flux dropped rapidly, causing increased statistical uncertainties of the measurements. The orange solid line in Fig. 5 results from a fit of the experimental cross sections employing the shape function for single-photon multiple ionization cross sections derived by Pattard [41].

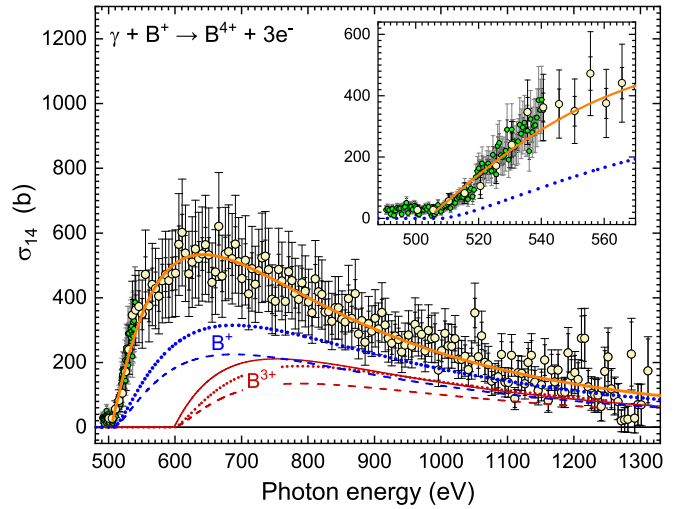


FIG. 5. Apparent cross sections for net triple photoionization of B^+ . The yellow-shaded circles were obtained in an overview scan, the green-shaded circles represent a threshold scan with smaller step sizes. The cross sections are shown with their statistical and total error bars. The orange solid line is a fit to the data with the function developed by Pattard for multiple photoionization [41]. The red-brown dotted line in the group labeled B^{3+} is the cross section for PDI of He-like B^{3+} [2]. The red-brown dashed line in that group results from the PDI model of Kheifets [16] and the red-brown solid line is the same curve multiplied by a factor of 1.4. The blue dashed line in the group labeled B^+ results from the PDI model and the blue dotted line is the same model cross section multiplied by 1.4. The inset shows a blow-up of the threshold region.

The total uncertainty of the normalization procedure is determined by the relative uncertainties of the calculated contributions to the model cross section $\sigma_{13}^{\text{model}}$ [see Eq. (6) and the discussion in the context of Fig. 2] plus the limitations of reproducibility of experimental conditions. The possible error of σ_{15}^{dir} is estimated to be $\pm 10\%$. For the contribution of the beam-fraction-weighted $K + L$ PDI cross sections an uncertainty of 100% was conservatively assumed. The reproducibility error is estimated to be $\pm 15\%$ as before in the present experimental campaign (see Refs. [1–3]). The resulting total uncertainty of each cross section is calculated as the quadrature sum of all the individual error bars including the statistical uncertainty.

Ab initio theory for describing double K -shell PDI of an atom or ion with more than three electrons is very complex and only few attempts are described in the literature [42,43]. The results of existing calculations are not satisfactory. No data are available for the B^+ ion. Southworth *et al.* faced the same problem in their investigation of double K -shell photoionization of the neutral Ne atom [44]. They argued that double K -shell photoionization of ten-electron neutral Ne can be modeled theoretically as PDI of two-electron (pure He-like) Ne^{8+} , disregarding the eight outer L -shell electrons altogether.

PDI of the He atom and He-like ions has been calculated previously (see Ref. [2] and references therein) using a number of different theoretical approaches which all give fairly consistent results. Southworth *et al.* used an R -matrix with

pseudostates (RMPS) approach to calculate the PDI cross sections for Ne^{8+} and found decent agreement with their measurements of double K -shell photoionization of neutral Ne. Following the same line of thought, we used the PDI cross section σ_{35} of He-like B^{3+} , recently obtained using CCC theory [2], as a proxy for double K -shell photoionization of the berylliumlike B^+ ion. This cross section is shown in Fig. 5 as the red-brown dotted line in the group of curves labeled B^{3+} . Obviously, σ_{35} does not reproduce the measurement of σ_{14} which has a substantially lower threshold. Different from the work of Southworth *et al.*, a shift of σ_{35} to the threshold of σ_{14} would not provide a satisfactory agreement with the experiment either.

The PDI model of Kheifets [16] used already for the calculation of $L + L$ and $K + L$ PDI cross sections in B^+ can also provide $K + K$ cross sections. As a test, double K -shell photoionization of helium-like B^{3+} was calculated using the model. The result is shown as the red-brown long-dashed curve in the group of lines labeled B^{3+} . Near the maximum, the model cross section is about 20% too low, while at higher photon energies the relative difference is a little larger. Multiplying the model cross section by a factor of 1.4 brings the result close to σ_{35} at higher energies but overshoots at lower energies, as shown by the red-brown solid line in Fig. 5.

As already mentioned, the PDI model can also be applied to $K + K$ PDI of the berylliumlike B^+ ion. The result is shown as the blue dashed line in the group of curves labeled B^+ . There is no difference between double K -shell PDI of B^+ ions in their ground state and of metastable B^+ . Applying the same correction factor of 1.4 as in the case of He-like B^{3+} produces the blue dotted line in the same group. At high energies, this line comes close to the measured data. A significantly higher correction factor would bring it above the experiment, and that would not make any sense for a contribution to σ_{14} . Even though the factor of 1.4 produces an overcorrection in the case of B^{3+} at lower energies, the corresponding, probably also overcorrected cross section for B^+ is still too small compared to the experimental cross-section maximum, even outside the very conservatively estimated total experimental uncertainties.

Two possible conclusions can be drawn from the comparisons in Fig. 5:

- (1) the PDI model is insufficient and delivers a cross section that does not fully match the double K -shell PDI cross-section curve either in shape or in height, and
- (2) there are nonvanishing contributions to the experimental σ_{14} beyond double K -shell ionization with subsequent autoionization.

The latter hypothesis is supported by the experimental data, as the inset of Fig. 5 with a blow-up of the threshold region shows. Below the apparent threshold of $K + K$ PDI at about 508 eV there is still a nonvanishing cross section of 20–30 b.

For further discussion of possible additional contributions to the experimentally determined cross section σ_{14} , the scaled (by a factor of 1.4) $K + K$ result of the PDI model for B^+ is subtracted from σ_{14} . The resulting cross-section function around the $1s + 1s$ PDI threshold is shown in Fig. 6. The cross-section difference $\sigma_{14} - \sigma_{1s+1s}$ is nonzero at energies below the $K + K$ thresholds of both metastable and ground-state B^+ , which clearly demonstrates contributions to σ_{14}

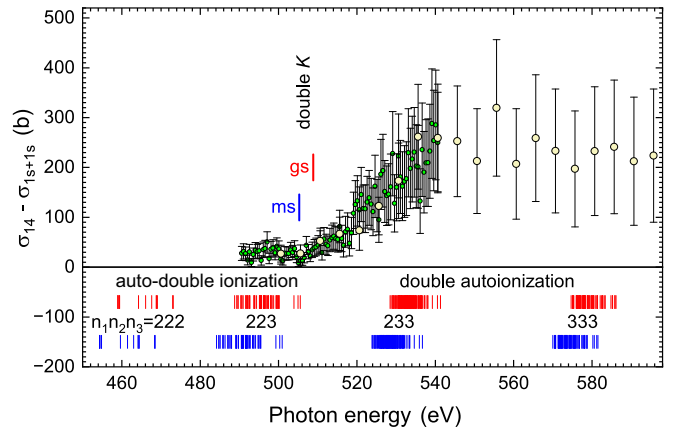


FIG. 6. Cross-section difference $\sigma_{14} - \sigma_{1s+1s}$ in the threshold region where the K -shell PDI cross section σ_{1s+1s} is obtained from the PDI model and multiplied by a factor of 1.4. The K -shell PDI thresholds of ground-state and metastable B^+ are shown as vertical bars above the data. Thresholds for K -shell ionization with K -shell excitation are displayed as vertical bars below the zero line. Thresholds for the metastable B^+ ions are shown as red vertical lines in the upper row, while thresholds for ground-level B^+ are shown as blue vertical lines in the lower row. Groups of thresholds are labeled by the principal quantum numbers of the three remaining electrons in excited states after K -shell ionization with K -shell excitation. The yellow-shaded and green-shaded circles result from the cross sections shown in Fig. 5 with identical symbols.

other than direct double K -shell ionization. Above the $K + K$ threshold, the difference cross section increases over a photon-energy range of about 40 eV and then drops off very slowly. This dropping off cannot be seen in Fig. 6 but follows from the energy dependences shown in Fig. 5 over a range of 800 eV.

The discussion at the beginning of the present section suggests that IE processes involving both K -shell electrons, in both metastable and ground-level B^+ , can contribute to σ_{14} at photon energies greater than about 460 eV. The flexible atomic code (FAC) of Gu [45] has been applied to calculate the thresholds for individual IE channels populating intermediate $2s\ 2\ell\ n\ell'$ or, more generally, $n_1\ell_1\ n_2\ell_2\ n_3\ell_3$ triply excited three-electron states of B^{2+} . Principal quantum numbers that may produce a contribution to σ_{14} are $n_1, n_2, n_3 \geq 2$. Levels with energies below the threshold for the production of $\text{B}^{3+}(2s\ n\ell)$ with $n = 2, \ell = 0, 1$, which is below the $K + K$ threshold, can only contribute to net triple ionization by double-Auger decays (termed auto-double ionization in Fig. 6), an expression commonly used in connection with similar resonances in electron-impact ionization of ions [46]. Levels above that threshold of about 508 eV may decay by sequential single-Auger processes (termed double autoionization [46] in Fig. 6). Sequential Auger decays are much more likely than simultaneous two-electron ejection. The sheer number of states that fulfill the condition for sequential Auger decay may explain the gradual increase of the observed cross section $\sigma_{14} - \sigma_{1s+1s}$. In this context, one should also keep in mind that the calculated energies may be slightly off the real IE thresholds.

IE processes involving both K -shell electrons were observed previously as a substantial contribution to net double photoionization of B^{2+} . The associated cross sections reached a size of up to approximately 1 kb. Here, we observe a cross section that reaches about 250 b at 540 eV. Considering the uncertainty of the cross section for double K -shell ionization of B^+ , the size of the extra cross section to which we assign the IE contribution to σ_{14} is of the right order of magnitude. Unfortunately, the CCC approach does not provide a quantitative assessment of the IE cross section of a four-electron atom or ion.

IV. SUMMARY

Single-photon double and triple ionization of berylliumlike B^+ have been studied in the energy range up to about 1300 eV. We show that the cross section for net double ionization is dominated by direct K -shell single ionization with subsequent Auger decay of the resulting K -shell vacancy. Higher-order contributions such as $L + L$ and $K + L$ direct double ionization were calculated and found to be negligible considering the total uncertainty of the experimentally determined cross section σ_{13} .

The first observation of a double- K -shell-vacancy state, the $2s^2 2p 3s \ ^1P_1$ resonance, in a berylliumlike ion is reported. The resonance energy agrees remarkably well with extensive, relativistic Hartree-Fock calculations. The resonance contributes to σ_{13} . It is formed by direct double K -shell excitation and predominantly decays via two sequential Auger processes, forming the final $B^{3+}(1s^2)$ ion.

Net triple photoionization of B^+ forming H-like B^{4+} ions is due to the creation of two K -shell vacancies, either by $K + K$ direct double ionization with subsequent Auger decay or by K -shell ionization accompanied by direct K -shell excitation with subsequent two-electron emission. This can only be a double-Augur process if a triply excited intermediate B^{2+} state is formed with an excitation energy (measured from the ground state of B^+) of less than about 508 eV, which is the

threshold for direct double K -shell ionization. Excited B^{2+} states with their threshold greater than 508 eV can also decay by two sequential single-Augur processes.

In summary, higher-order ionization processes triggered by single-photon absorption and driven by electron-electron correlation have been studied both experimentally and theoretically. Such processes dominate the multiple-ionization cross sections of berylliumlike B^+ ions at energies far beyond the K edge.

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DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

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