Observation of four-electron Auger processes

A Müller1, A Borovik Jr.1, T Buhr1,2, J Hellhund1, K Holste1,3, A L D Kilcoyne4, S Klumpp5, M Martins5, S Ricz1,6, J Viefhaus7, S Schippers1,3

1 Institut für Atom- und Molekülphysik, Justus-Liebig-Universität Giessen, 35392 Giessen, Germany
2 Physikalisch-Technische Bundesanstalt, 38116 Braunschweig, Germany
3 I. Physikalisches Institut, Justus-Liebig-Universität Giessen, 35392 Giessen, Germany
4 Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720-8225, USA
5 Institut für Experimentalphysik, Universität Hamburg, 22761 Hamburg, Germany
6 Institute for Nuclear Research, Hungarian Academy of Sciences, 4001 Debrecen, Hungary
7 FS-PE, DESY, 22607 Hamburg, Germany

E-mail: Alfred.Mueller@iamp.physik.uni-giessen.de

Abstract. Multiple ionization of ions subsequent to absorption of a single photon has been studied employing a photon-ion merged-beam setup at the PETRA III synchrotron radiation facility of DESY in Hamburg. Absolute cross sections for single, double and triple ionization of C+ ions were measured with emphasis on specific well defined terms of K-shell excited C+. In particular, the terms C+(1s2s22p2 2D,2P) were excited from the ground level of C+. Subsequent autoionization processes resulted in the production of C2+, C3+ and C4+ ions. The associated decay mechanisms are single-Auger, double-Auger and triple-Auger decay. The observation of C4+ products arising from C+(1s2s22p2 2D,2P) unambiguously confirmed the existence of triple-Auger decay, i.e., a process in which 4 electrons interact with one another such that one fills the K-shell vacancy and the others are simultaneously ejected. The experiment yields branching ratios for the Auger decay channels as well as individual decay rates for autoionization and radiative stabilization of the C+(1s2s22p2 2D,2P) terms.

1. Introduction

Multi-electron processes associated with electron-electron interactions or electron correlations have always attracted broad interest since the early days of quantum mechanics. Free helium atoms and He-like ions provide the minimum number of electrons necessary for electron correlation effects to occur. These effects crucially determine the atomic structure of any He-like system as well as the decay probabilities of its excited states. The most important decay mechanism of doubly excited He or, more general, multiply excited atomic systems with two or more electrons is the Auger process [1] in which two electrons exchange energy so that one drops down into a lower bound state while the second electron escapes to the continuum and carries away the excess energy which is characteristic for each transition.

Higher-order Auger decay processes are also possible and have been observed in numerous electron-ion and photon-ion interactions [2–4]. Next in level of complexity after the single-Auger process [1] are Auger mechanisms in which three electrons interact with one another, one filling a core hole and two electrons being promoted to excited states or to the continuum. Such
mechanisms were discovered already half a century ago by Carlson and Krause [5] who identified
double-Auger processes where one electron undergoes a transition to a deep atomic shell while
the other two electrons are emitted simultaneously sharing the excess energy.

Recently, an unambiguous observation of triple-Auger decay processes [6] has been reported.
Singly charged carbon ions were irradiated with photons of an energy suitable for excitation of a
K-shell electron to the L shell. The intermediate C\(^{+}\) K-vacancy state with four electrons in the
L-shell was observed to decay to C\(^{4+}\). The only decay mechanism by which this experimental
observation can be explained is the simultaneous ejection of three electrons while the fourth
electron falls down into the initially prepared vacancy in the K shell. Fig. 1 illustrates the
formation and the decay of an excited level in the observed process.

2. Brief overview of the experiment
The experiment was carried out employing the photon-ion merged-beam setup PIPE\(^{1}\) at the
world’s presently brightest third-generation synchrotron-radiation source, PETRA III, which
is located on the site of DESY in Hamburg. PIPE [7] is the permanent endstation of the
"Variable Polarization XUV Beamline" P04 [8]. The layout of PIPE is shown in Fig. 2. Ions are
produced by suitable, interchangable sources installed on a high-voltage platform. The beam
of accelerated ions is transported to a 90° analysing magnet by which the desired ion species
is selected. The purified ion beam is then directed to the axis of the photon beam so that the
two counterpropagating beams overlap one another in the merged-beam section. Photoions are
separated from the parent ion beam with the demerging magnet and directed to a single particle
detector. In the merged-beam section the spatial overlap of the two beams is quantified by a form
factor [9] which is obtained by probing the two-dimensional profiles of the beams with six slit
scanners at three different axial positions [7]. By normalizing the signal count rate to the ion flux
measured in a large Faraday Cup inside the demerger chamber, to the photon flux measured
with a photodiode and to the form factor, absolute cross sections for photodisintegration of
atoms or molecules can be determined.

For the present measurements an all-permanent-magnet electron-cyclotron-resonance (ECR)
ion source was employed to produce C\(^{+}\) ions from methane gas. Pure \(^{12}\)C\(^{+}\) beams of up to 63 nA
were measured in the demerger Faraday cup. The overlap form factors were between 3500 cm\(^{-1}\)

\(^{1}\) Photon-Ion spectrometer at PETRA III
Figure 2. Sketch of the photon-ion merged-beam setup PIPE used in the present experiments. Ions enter from the left (red arrow), photons from the right (blue arrow). The two beams can be made to interact in the merged-beam (MB) section or in the crossed-beam (CB) section. FC: Faraday cup, AM: analysing magnet, SD: spherical deflector, DM: demerging magnet, SPD: single-particle detector, PD: photodiode.

and 9900 cm$^{-1}$ depending on the degree of ion-beam collimation. The available photon flux ranged from $2 \times 10^{11}$ s$^{-1}$ at 288 eV and 16 meV bandwidth to $1.2 \times 10^{13}$ s$^{-1}$ at 315 eV and 130 meV bandwidth. Under such extremely favorable conditions high-resolution measurements were carried out for single ionization of C$^+$ ions with resolving powers up to 18,000 thus allowing for the determination of natural line widths of some of the strongest photoexcitation resonances. Alternatively, with less energy resolution but much higher photon flux, processes with extremely small cross sections down to the region of 5 kb became accessible. The photon energy axis was calibrated to within ±30 meV by remeasuring the resonance energies in the photoionization of C$_3^+$ ions known from a previous experiment [10].

3. Experimental results

Absolute cross sections for processes $\gamma + C^+(1s^22s^22p^2\,^2P) \rightarrow C^+(1s^22p^2\,^2D,\,^2P) \rightarrow C^{(1+m)+}(1s^22p^{2\ell^2-m}) + me$ leading to net photoionization with $m = 1, 2, 3$ were determined. Fig. 3 shows the measured cross section for photon-induced single ionization of C$^+$ ions in a narrow photon energy range where C$^+$($1s^22p^2\,^2D,\,^2P$) terms can be excited from the C$^+$($1s^22s^22p^2\,^2P$) ground term. The measurements were carried out with a monochromatized photon beam (with energy $E_\gamma$) at fixed bandwidth $\Delta E_\gamma = 16$ meV. With the associated resolving power $E_\gamma/\Delta E_\gamma \approx 18000$ it was possible to determine the natural widths of the two resonances to be $(101 \pm 3)$ meV and $(49.3 \pm 2)$ meV, respectively. These widths are slightly lower than the results of a previous measurement [11]. They have uncertainties which are factors of 3 to 5 smaller than the error bars of the previous data.

Since the cross sections are on an absolute scale the areas under the two peaks shown in Fig. 3, i. e., the strengths of the associated resonances, can be determined. They are $(13.1 \pm 2.0)$ Mb eV for the $^2D$ term and $(21.4 \pm 3.2)$ Mb eV for the $^2P$ term. Before drawing further conclusions from these numbers one has to consider the presence of metastable C$^+$($1s^22s^22p^2\,^2P$) in the parent ion beam. The fraction of such long-lived excited parent ions was determined [6] to be 10% with an estimated uncertainty of 5%. The resonance areas have to be modified accordingly. The corrected numbers for the two resonance strengths of interest
oscillator strengths for absorption the transition rates of calculations using the Cowan code [13, 14] in configuration-interaction (CI) mode. From the \( k \) from the excited term \((1 \rightarrow i)\) to the two resonances of interest the oscillator strengths are inferred [12]. The measured natural linewidths \( \Gamma \) yield the lifetimes of the \( C \) are typically smaller than the size of the experimental points. The solid line is a fit of two Voigt line profiles to the observed resonances which are associated with K-shell excited terms \( 1s2s^22p^2 \, \ ^2D, ^2P \) and their single-Auger decay.

\[
S(2P \rightarrow ^2D) = (14.6 \pm 2.2) \text{ Mb eV} \text{ and } S(2P \rightarrow ^2P) = (23.8 \pm 3.6) \text{ Mb eV}.
\]

From the data displayed in Fig. 3 information about transition probabilities and lifetimes can be inferred [12]. The measured natural linewidths \( \Gamma \) yield the lifetimes \( \tau = \frac{1}{\Gamma} \) of the \( C^+(1s2s^22p^2 \, ^2D) \) and \( C^+(1s2s^22p^2 \, ^2P) \) resonances to be \((6.5 \pm 0.2) \times 10^{-15} \text{ s} \) and \((1.34 \pm 0.05) \times 10^{-14} \text{ s} \), respectively. The associated total transition rates are \( A = \frac{1}{\tau} = 1.5 \times 10^{14} \text{ s}^{-1} \text{ and } 7.5 \times 10^{13} \text{ s}^{-1} \), respectively. The measured resonance strengths yield the absorption oscillator strengths \( f_a = 9.11 \times 10^{-3} \, S \). For the transitions from the ground level to the two resonances of interest the oscillator strengths are \( f_a(2P \rightarrow ^2D) = 0.133 \pm 0.020 \) and \( f_a(2P \rightarrow ^2P) = 0.217 \pm 0.033 \) in perfect agreement with the results \((0.129 \text{ and } 0.225, \text{ respectively})\) of calculations using the Cowan code [13, 14] in configuration-interaction (CI) mode. From the oscillator strengths for absorption the transition rates \( A(k \rightarrow i) \) for electromagnetic transitions from the excited term \((k)\) to the ground term \((i)\) can be obtained

\[
f_a(i \rightarrow k) = 1.4992 \times 10^{-14} \lambda_{ki}^2 \frac{g_k}{g_i} A(k \rightarrow i) ,
\]

where \( \lambda_{ki} \) is the wavelength of the transition photon in units of nm, \( g_k \) and \( g_i \) are the statistical weights of levels \( k \) and \( i \), respectively, and \( A(k \rightarrow i) \) is in units \( \text{s}^{-1} \). With the oscillator strengths determined in the present experiment the transition rates are \( A(2D \rightarrow ^2P) = (2.88 \times 10^{11}) \text{ s}^{-1} \) and \( A(2P \rightarrow ^2P) = (8.16 \times 10^{11}) \text{ s}^{-1} \). These rates for electromagnetic transitions are very much smaller than the total transition rates. Hence, the competing Auger transition rates determine the natural widths of the K-vacancy terms while the electromagnetic transition rates are negligible when considering the experimental uncertainties.

Figure 3. Experimental cross sections for single ionization of a \( C^+ \) ion by a single photon measured with an energy bandwidth of approximately 16 meV. The statistical error bars are typically smaller than the size of the experimental points. The solid line is a fit of two Voigt line profiles to the observed resonances which are associated with K-shell excited terms \( 1s2s^22p^2 \, ^2D, ^2P \) and their single-Auger decay.
Figure 4. Experimental cross sections for triple ionization of a $C^+$ ion by a single photon measured with an energy bandwidth of approximately 92 meV. The statistical error bars are indicated. The solid line is a fit of two Voigt line profiles to the observed resonances which are associated with K-shell excited terms $1s^22s^22p^2 2D, 2P$ and their triple-Auger decay.

Figure 5. Relative probabilities for single-, double- and triple-Auger decay of K-shell excited $C^+(1s^22s^22p^2 2D)$ and $C^+(1s^22s^22p^2 2P)$. The probability for single-Auger decay is set to 1.

The ratios of resonance strengths contained in the double- and single-ionization peaks are 0.0266 for the $2D$ resonance and 0.0333 for the $2P$ resonance. These ratios can be interpreted as the probabilities of double-Auger relative to single-Auger decay.

The outstanding brightness of the photon beam provided at beamline P04 of PETRA III together with the efficient suppression of background in the PIPE experiment made possible to measure also triple ionization of $C^+$ ions. The resulting absolute cross sections obtained for the $C^+(1s^22s^22p^2 2D)$ and $C^+(1s^22s^22p^2 2P)$ resonances are shown in Fig. 4. The energy resolution was 92 meV. The total uncertainty of the cross sections is estimated to be $\pm 50\%$.

The ratios of resonance strengths contained in the triple- and single-ionization peaks (see Fig. 3) are $1.31 \times 10^{-4}$ for the $2D$ resonance and $1.33 \times 10^{-4}$ for the $2P$ resonance. These ratios can be interpreted as the probabilities of triple-Auger relative to single-Auger decay.

By combining the information about the relative decay probabilities discussed above with the total Auger-decay rate inferred from the single-ionization measurements (see Fig. 3) it is...
possible to provide absolute transition rates. The triple-Auger decay rate was found to be \(1.92 \times 10^{10} \text{s}^{-1}\) for the \(\text{C}^+ (1s^2 2s^2 2p^2 2D)\) and \(9.68 \times 10^9 \text{s}^{-1}\) for the \(\text{C}^+ (1s^2 2s^2 2p^2 2P)\) intermediate resonantly-excited terms investigated in this study. Both decay rates are estimated to have a 50% uncertainty. The ratios of single- to double- to triple-Auger rates of the \(2^D\) and \(2^P\) terms are about 100 : 2.7 : 0.013 and 100 : 3.3 : 0.013, respectively. These ratios are illustrated in Fig. 5.

4. Summary

In summary, the possibility to work at PIPE with singly or multiply charged ions facilitated the choice of a suitable atomic system, boronlike \(\text{C}^+\), for unambiguous demonstration of the triple-Auger decay process. By selectively populating the energetically lowest levels of K-shell-excited \(\text{C}^+\) and observing triple ionization to \(\text{C}^{4+}\) it is clear that the initial K vacancy must have been filled, i. e., no electrons were left in the L shell ruling out any cascade process and leaving triple-Auger decay as the only possible mechanism. By the measurement of absolute cross sections for single, double and triple ionization of \(\text{C}^+\) and by determining the natural widths of the selected intermediate K-shell excited terms, the absolute decay rates of triple-Auger processes could be inferred.

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