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Topical Review

Multiple photodetachment of atomic anions via single and double core-hole creation

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Abstract

We review the recent experimental and theoretical progress in *K*-shell detachment studies of atomic anions. On the experimental side, this field has largely benefitted from technical advances at 3rd generation synchrotron radiation sources. For multiple detachment of C^- , O^- , and F^- ions, recent results were obtained at the photon-ion merged-beams setup PIPE which is a permanent end station at beamline P04 of the PETRA III synchrotron light source in Hamburg, Germany. In addition to a much increased photon flux as compared to what was available previously, the PIPE setup has an extraordinary detection sensitivity for heavy charged reaction products that allows one to study detachment processes with extremely low cross sections in the kilobarn range, e.g., for processes involving the simultaneous creation of two core-holes by a single photon as observed in the net triple detachment of F^- and the net five-fold detachment of C^- . Moreover, hitherto disregarded photodetachment resonances have been discovered, which exhibit a variety of line shapes. For O^- the core-hole lifetime could be determined precisely from a high-resolution measurement of a photodetachment resonance. These experimental findings pose new challenges for state-of-the-art atomic theory and require calculations combining photoexcitation (ionization) with decay cascade processes that follow after initial core-hole production.

Keywords: inner-shell photodetachment, merged-beams method, synchrotron radiation, atomic anions, double core-hole creation

(Some figures may appear in colour only in the online journal)

1. Introduction

Negative atomic ions are of great fundamental interest since they are peculiar atomic systems where exclusively correlation

effects lead to the binding of the extra electron to the neutral atom. This makes negative ions (anions) an ideal testing ground for atomic theory. Experimentally, much work has been done on photodetachment of the outer electron using tunable lasers as intense photon sources for measuring, e.g., the threshold behaviour of photodetachment cross sections, resonance features, or photo-electron energy and angular distributions. These and other topics related to atomic anions have been

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comprehensively reviewed already more than a decade ago [1, 2]. Since then, refined experimental methods have yielded a number of new precision results, e.g., on electron binding energies and transition rates (see [3–7] for the latest developments on the photodetachment of valence electrons).

This topical review focusses on the photodetachment of the innermost, i.e., the *K*-shell electrons of atomic anions. This poses extra challenges for atomic theory since, upon the creation of the core holes, the valence electrons are then subject to relaxation mediated by strong many-electron effects [8, 9]. Experimental work on inner-shell photodetachment of negative ions is scarce. Prior to the work reviewed here, photodetachment via the creation of a single *K*-hole has been experimentally studied only for a limited number of light anions up to O^- [10–15]. In these studies only double detachment has been considered, and this only for rather narrow energy ranges around the respective *K*-shell detachment thresholds. Further work on inner-shell photodetachment addressed the *L*, *M* and *N* shells of heavier atomic anions [16–25]. All these measurements were carried out mostly more than a decade ago using the photon-ion merged-beams technique [26, 27] (see below) at 3rd generation synchrotron light sources. At that time, the photon flux was considerably lower than what is currently available.

Here, we summarize the significant experimental progress that was recently achieved on multiple photodetachment via *K*-shell excitation and ionisation of C^- [28], O^- [9], and F^- [29] ions at a high photon-flux beamline of a modern 3rd generation synchrotron in combination with intense ion beams as well as sensitive and selective ion-detection techniques. This topical review is organized as follows. Section 2 provides a brief description of the photon-ion merged-beams technique. Experimental findings on inner-shell photodetachment of atomic anions are presented and discussed in section 3. Corresponding theoretical developments are presented in section 4. Section 5 provides conclusions and a brief outlook.

2. The photon-ion merged-beams technique

Experiments with ionic targets are challenging because of the low target densities which are usually orders of magnitude smaller than the typical densities of neutral gas targets. The photon-ion merged-beams method (see [27] for a recent introductory review) compensates the low target density by providing an elongated interaction region of typical ~ 1 m length where the photon beam and the ion beam move coaxially. In addition, heavy charged reaction products can be collected and detected with nearly 100% efficiency, since they move with keV energies and can be easily separated from the primary beam by electric or magnetic fields. Nevertheless the signal rates from such an arrangement are still quite small, such that meaningful experiments with UV and x-ray photons could only be carried out after the advent of 2nd generation synchrotron light sources. Pioneering work was carried out at the Daresbury Synchrotron Radiation Source [30]. Since then, the technique spread to other synchrotron radiation sources, e.g., ASTRID [31], SPring-8 [32], ALS [33], and SOLEIL [34, 35]. Because of their rather large size (heavy magnets

and ion sources) these ion-beam setups were realized as permanent installations and, hence, the available photon-energy range depends on the chosen photon beam line.

The latest development in this field is the Photon-Ion spectrometer at PETRA III (PIPE) [36, 37] (figure 1) which has been set up by a consortium of German university groups at the photon beamline P04 [38] of the PETRA III synchrotron operated by DESY in Hamburg, Germany. The PIPE setup is unique with respect to the available photon flux and photon energy range. PIPE is the only photon-ion merged-beams setup where photon energies higher than 1000 eV, i.e., up to nearly 3000 eV are available. The record-high photon flux at the photon beamline P04 reaches up to several 10^{14} s^{-1} depending on photon energy and resolving power.

The PIPE setup features an ion-source platform where user-supplied ion sources can be easily installed such that the optimal source for a given ion species can be operated. The most recent addition is a Cs-sputter ion source for the production of intense beams of negatively charged ions which has been used for the experiment with C^- ions discussed below [28]. This source had not been available for the previous experiments with O^- [9] and F^- [29] ions where an electron-cyclotron-resonance (ECR) ion source was used with negative ion currents that were an order of magnitude lower than the C^- ion current from the Cs-sputter ion source.

A salient feature of the photon-ion merged-beams method is its ability to provide absolute cross-section data which are important, e.g., for applications in plasma physics and astrophysics. For providing such data, the measured count rate of the reaction product under consideration is normalized on ion current, photon flux and detection efficiency. In addition, the mutual spatial overlap between the ion beam and the photon beam has to be determined. At PIPE, three sets of slit scanners serve this purpose. The entire procedure, which is described in detail in [36], gives rise to a systematic uncertainty of the resulting absolute cross section scale that amounts to typically $\pm 15\%$.

The photon energy scale of the PETRA III photon beamline P04 can be calibrated by comparing absorption measurements in gases with previously established reference standards from the literature [37]. The systematic uncertainty of the photon-energy scale that results from this procedure is typically about ± 200 meV. This rather large error is directly related to the uncertainties of the reference standards in the XUV photon-energy range. Based on measurements at PIPE, it has recently been suggested that photoionisation resonances of few-electron ions can potentially serve as much more accurate reference standards [39]. Corresponding activities are ongoing.

The PIPE setup has lead to a breakthrough in experimental sensitivity, which allows for much more detailed studies of inner-shell ionisation/detachment of ionic targets than was possible before [40–42]. The results from the first five years of operation of the PIPE setup have been summarized in [43]. Apart from inner-shell photodetachment and photoionisation of negatively and positively charged atomic ions also photo-processes involving molecular ions, and positively and negatively charged endohedral fullerene ions have been

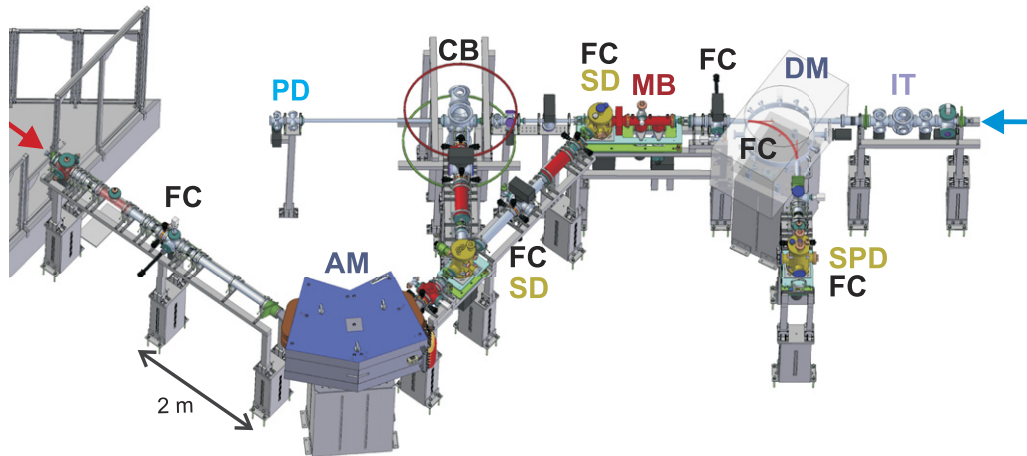


Figure 1. Sketch of the photon-ion merged-beams setup PIPE (see [36] for details). The labelled items are photodiode (PD), analysing magnet (AM), spherical deflectors (SD), crossed-beams interaction point (CB), merged-beams interaction region (MB), demerging magnet (DM), single-particle detector (SPD), Faraday cups (FC), and ion trap (IT). Reproduced from [36]. © IOP Publishing Ltd. All rights reserved.

investigated (see [44–46] for the most recent corresponding results).

3. Experimental findings

Figure 2 bears witness to the significant progress that has been achieved at PIPE. The main panel of this figure displays cross sections σ_m for net m -fold detachment

$$h\nu + C^- \rightarrow C^{(m-1)+} + me^-, \quad (1)$$

which were measured for $m = 2$ –5 with low statistical uncertainties over extended energy ranges (for σ_5 see figure 5). The new data exhibit a wealth of previously unknown thresholds and resonances as compared to the previously available result for double-detachment of $C^-(1s^2 2s^2 2p^3 \ ^4S)$ [14]. These previous results are depicted in the left inset of figure 2. Obviously, the data from PIPE represent a new standard for inner-shell detachment studies with atomic anions.

3.1. Near K -threshold resonances

The earlier study by Walter *et al* [14] focussed on the $1s 2s^2 2p^4 \ ^4P$ resonance near the K threshold which was measured with a photon-energy spread of ~ 120 meV. This is about a factor 4 lower than the 500 meV energy spread of the photon beam used by Perry-Sassmannshausen *et al* [28]. Consequently, the resonance cross section is a factor of ~ 4 higher in the data of Walter *et al* as compared to the double-detachment data of Perry-Sassmannshausen *et al*. As expected, the integrated resonance strengths of 8.2 ± 3.2 Mb eV and of 6.8 ± 1.0 Mb eV, respectively, agree with each other within the rather large uncertainty of the earlier result.

Because of the narrow energy spread in their experiment, Walter *et al* [14] were able to extract the resonance width of the $1s 2s^2 2p^4 \ ^4P$ resonance from their measurement. To this end, they fitted a Breit-Wigner line shape [49] to the experimental data points. This line shape is a function of the photon energy E and is parameterized by the K -shell detachment threshold

energy E_{th} , the resonance energy E_r , and the resonance width Γ as follows:

$$\sigma(E) = \begin{cases} \sigma_0 & \text{for } E \leq E_{th} \\ \sigma_0 + \frac{A(E - E_{th})^{3/2}}{(E - E_r)^2 + (\Gamma/2)^2} & \text{for } E > E_{th} \end{cases} \quad (2)$$

with σ_0 and A being an energy-independent background cross section and a scaling constant, respectively. The result of the fit is displayed as a full line in the left inset of figure 2. It agrees very well with the experimental data despite of the fact that equation (2) does not account for the experimental energy spread. As already mentioned by Walter *et al*, the extracted line width $\Gamma = 0.11 \pm 0.04$ eV must therefore be considered as an upper limit. Apart from an insignificant 0.25 eV energy shift (see caption of figure 2), the new double-detachment data from PIPE [28] confirm the earlier findings of Walter *et al* [14].

The detailed investigation of near K -threshold resonances had also motivated the previous inner-shell studies with $Li^-(1s^2 2s^2 \ ^1S)$ [10, 11], $B^-(1s^2 2s^2 2p \ ^2P)$ [12] and $O^-(1s^2 2s^2 2p^5 \ ^2P)$ [15] where double-detachment cross sections were measured over very narrow energy ranges in a similar manner as depicted in the left inset of figure 2 for C^- [14]. Breit-Wigner line shapes were also found for the near K -threshold resonances of $B^-(1s^2 2s^2 2p \ ^2P)$ [12]. For Li^- the experimental resolving power was not sufficient for a detailed analysis of resonance line shapes. The same holds for the O^- data from the ALS [15].

Figure 3 presents the O^- data from PIPE [9]. As mentioned in section 2, an ECR ion source was used, although this type of ion source is less suitable for the production of O^- ions than a Cs-sputter source. Nevertheless, absolute cross sections for net double and triple detachment could be measured. In both cross sections, the $1s 2s^2 2p^6 \ ^2S$ resonance at 525.6 eV is prominently visible together with the threshold for direct detachment of a $1s$ electron which sets in at about 529.6 eV. The line-shape of the $1s 2s^2 2p^6 \ ^2S$ resonance turned out to be purely Lorentzian as revealed by a high-resolution scan (inset

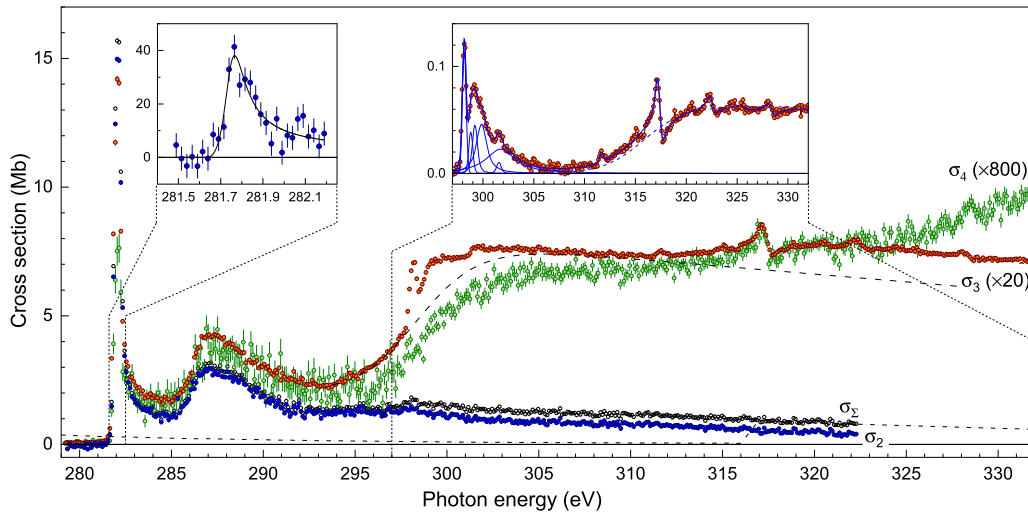


Figure 2. Absolute cross sections σ_m for m -fold detachment of C^- ions [28], that were measured with the PIPE setup at the XUV beamline P04 of the PETRA III synchrotron light source. The blue, orange and green symbols represent the measured absolute cross sections for $m = 2, 3$, and 4, respectively. The open symbols represent the sum cross section $\sigma_\Sigma = \sigma_2 + \sigma_3 + \sigma_4$. The black dash-dotted line is the absorption cross section of neutral carbon according to Henke *et al* [47]. The left inset shows the earlier result of Walter *et al* [14] for double detachment in the vicinity of the K -shell detachment threshold that was obtained at beamline 10.0.1 of the Advanced Light Source (ALS, Berkeley, USA). It should be noted, that the energy scale of the ALS experiment appears to be shifted by -0.25 eV as compared to the energy scale of the PIPE experiment. However, this shift is within the mutual uncertainties of both energy scales. The right inset displays the cross-section difference between the measured cross section σ_3 for net triple detachment of C^- and the dashed line that is displayed in the main panel of this figure. The thick solid line results from a resonance fit to the experimental data. In the fit, the resonance features were represented by Lorentzian and Fano line shapes convolved with a Gaussian that accounts for the experimental photon energy spread [48]. The fitted resonance parameters are provided in reference [28]. (a) Reprinted figure with permission from [14], Copyright 2006 by the American Physical Society. (b) Reprinted figure with permission from [28], Copyright 2020 by the American Physical Society.

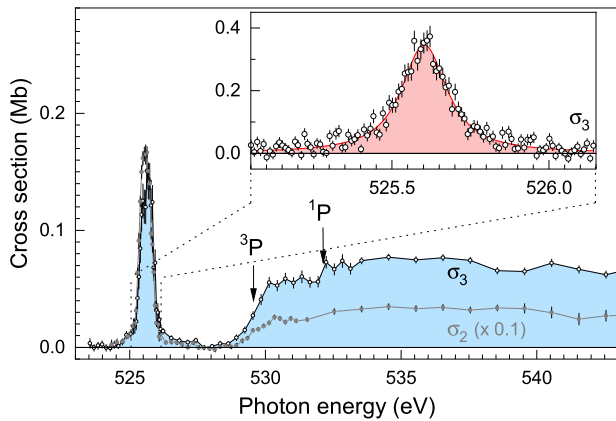


Figure 3. Measured cross sections σ_2 (gray-shaded circles) and σ_3 (open symbols, shaded curves) for double and triple detachment, respectively, of $O^-(1s^2 2s^2 2p^5 {}^3P)$ ions by single-photon impact [9]. The vertical arrows mark the positions of the $1s 2s^2 2p^5 {}^3P$ and $1s 2s^2 2p^5 {}^1P$ detachment thresholds at about 529.6 and 532.1 eV, respectively. The inset shows a Voigt line profile (full line) that has been fitted to high-resolution experimental data (open symbols). Reproduced from [43]. CC BY 4.0.

of figure 3). The experimental photon energy spread $\Delta E = 40$ meV corresponds to a resolving power $E/\Delta E \approx 13.000$. The natural line width was obtained by fitting a Voigt line profile to the measured data points. This resulted in $\Gamma = 0.164 \pm 0.014$ eV or a core-hole lifetime of 4.0 ± 0.3 fs.

Finally, let us note that the experimental photodetachment cross sections of $F^-(1s^2 2s^2 2p^6 {}^1S)$ at the given experimental

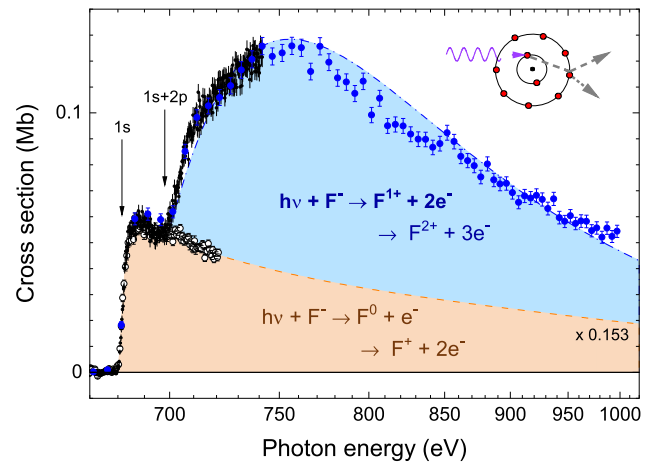


Figure 4. Measured absolute cross sections for double detachment (open symbols, scaled by an overall factor of 0.153) and triple detachment (small black and large blue full symbols) of F^- ions by single-photon impact [29]. Reproduced from [43]. CC BY 4.0.

sensitivity do not exhibit any resonance structure [29] (figure 4). This is attributed to the closed-shell structure of this particular anion.

3.2. Higher-energy thresholds and resonances

While all previous K -shell detachment experiments with atomic anions were confined to net double detachment in very narrow energy ranges at the K -shell detachment threshold (see, e.g., left inset of figure 2), the PIPE data comprise in

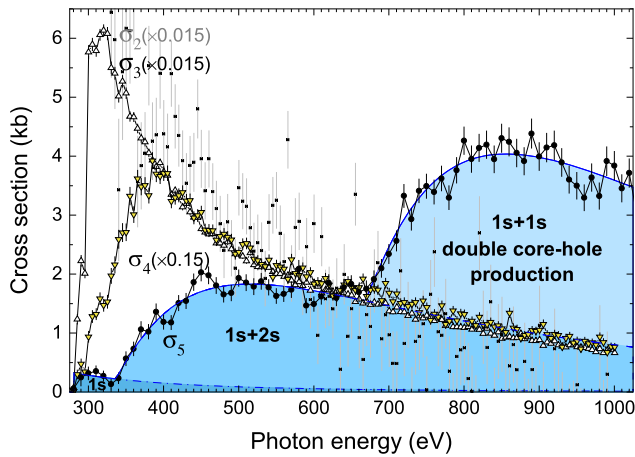


Figure 5. Measured cross sections σ_m for m -fold detachment ($m = 2-5$) of C^- ions for energies to beyond the threshold for double K -shell detachment [28]. The DPI cross sections were modelled with equation (3) using the parameters from table 1. Reprinted figure with permission from [28], Copyright 2020 by the American Physical Society.

addition to double detachment also triple, four-fold, and five-fold detachment. These data also extend over much wider ranges of photon energies (figures 2, 4 and 5). In these extended energy ranges numerous threshold and resonance features have been discovered which had not been discussed in the previously available literature despite of the fact that the atomic systems under investigation are rather fundamental. Of course, this disregard is related to the hitherto restricted availability of corresponding experimental data.

Already the still relatively limited O^- data exhibit an additional threshold feature which is particularly strong in the triple-detachment channel (figure 3). Apart from the lowest threshold for direct detachment of a $1s$ electron at 529.6 eV a weaker second threshold is visible in the triple-detachment channel at 532.1 eV. These two thresholds are associated with the fine structure of the excited (neutral) atom with a detached $1s$ -electron. The respective core-hole terms are $1s2s^22p^5^3P$ and $1s2s^22p^5^1P$ as indicated in figure 3.

For C^- , the thresholds for direct $1s$ -detachment are hidden below the strong resonances in the energy range 281–293 eV (figure 2). In fact, quantum mechanical interference between direct and resonant detachment causes the observed asymmetric line shape (equation (2)) of the $1s2s^22p^4^4P$ resonance discussed above. The second, broad resonance feature at ~ 287 eV is probably a blend of several individually unresolved resonances associated with $1s \rightarrow 3p$ excitations as suggested by detailed atomic-structure calculations [28] (see also section 4). This resonance is visible in all partial cross sections σ_m that are displayed in figure 2.

At energies above 293 eV, the cross section for net double detachment of C^- stays nearly constant until 298 eV and from then on decreases monotonically. In contrast, the triple and four-fold detachment cross sections exhibit a pronounced rise that sets in at 295 eV and continues up to 305 eV. This rise is associated with an initial detachment process where one $1s$ electron and one $2p$ electron are removed by a single photon. The subsequent filling of the resulting K -shell holes by Auger

processes leads to the emission of one or more electrons, such that the initial direct double ionisation event reveals itself only in the net triple and four-fold detachment cross sections and not in the cross section for net double detachment. Direct double core-hole creation will be discussed further in section 3.3 below.

Above the threshold for $1s + 2p$ direct double detachment (and subsequent autoionisation) a number of further resonances appear in particular in the cross section for net triple detachment of C^- . These resonances are magnified in the right inset of figure 2 which also displays the results of a resonance fit. This fit also suggests another threshold at ~ 315 eV. At present, a reliable designation of all the fitted features is not at hand, and only the pronounced Fano resonance at 317.3 eV has been tentatively assigned to the $1s2s(^3S)2p^3(^4P)3s(^3P)3p^4P$ term which can be reached by a double-excitation process of the $C^-(1s^22s^22p^3^4S)$ ground term [28].

In addition to the partial cross sections σ_m for $m = 2, 3, 4$, figure 2 also displays the sum cross section $\sigma_\Sigma = \sigma_2 + \sigma_3 + \sigma_4$. It can be argued that, at energies above the K -shell detachment threshold, this sum cross section largely corresponds to the C^- absorption cross section. At these energies, net single detachment is negligible since the K -hole levels in light ions decay practically exclusively via Auger processes leading to the ejection of further electrons. It should be noted that net single detachment cannot be easily observed by the photon-ion merged-beams technique since this requires the detection of neutral reaction products that propagate along the photon-beam axis. In any case, for energies above the threshold for direct $1s$ ionisation of neutral carbon at ~ 316.5 eV, σ_Σ is found to agree excellently with the photoabsorption cross section of neutral atomic carbon [47] which is also displayed in figure 2. Obviously, the extra electron of C^- does not have a significant influence on the high-energy absorption cross section. At lower energies the absorption is dominated by outer-shell processes that primarily lead to (not measured) single detachment.

3.3. Multiple detachment via double core-hole creation

The fundamental process of direct double photoionisation (DPI), i.e., the removal of two electrons by a single photon, is extremely sensitive to the details of the electron–electron interaction. Therefore, it has been a central topic of atomic physics already for decades (see, e.g., [50–56] and references therein). Moreover, double core-hole production in atoms and molecules is currently an active topic particularly at VUV and x-ray free-electron lasers [57–66].

Inner-shell DPI has been addressed recently in a photodetachment experiment with F^- anions [29]. Figure 4 displays absolute cross sections for net double and triple detachment of F^- . As already mentioned above, these cross sections are free from any contributions by resonances. However, the triple-detachment cross section exhibits a clear signature for the simultaneous knock out of a $1s$ and a $2p$ electron by a single photon: above a threshold energy of about 700 eV, the associated cross section appears on top of a continuously decreasing ‘background’ which is due to single core-hole creation and subsequent emission of two Auger electrons. This background

Table 1. DPI parameters as obtained from fitting equation (3) to the experimental cross sections for net triple photodetachment of F^- [29] (figure 4) and for net five-fold photodetachment of C^- [28] (figure 5). For C^- , the Wannier exponent α [68] was fixed to the value for the doubly detached intermediate C^+ ion.

Ion	Electrons removed	E_{th} (eV)	E_M (eV)	σ_M (kb)	α
F^-	$1s + 2p$	698.7	763.1	95	1.1
C^-	$1s + 2s$	336	524	1.75	1.1269
C^-	$1s + 1s$	668	891	3.00	1.1269

(dashed curve in figure 4) has been modelled on the basis of the separately measured cross section for net double detachment.

The dash-dotted curve in figure 4 is the sum of the ‘background’ and an estimated cross section for $1s + 2p$ DPI. The latter has been calculated with the empirical formula developed by Pattard [67], i.e.,

$$\sigma(E) = \sigma_M x^\alpha \left(\frac{\alpha + 7/2}{x\alpha + 7/2} \right)^{\alpha+7/2}, \quad x = \frac{E - E_{th}}{E_M - E_{th}}, \quad (3)$$

which parameterizes the DPI cross section in terms of the Wannier exponent α [68] and the cross section maximum σ_M , which occurs at the energy E_M . For $1s + 2p$ DPI of F^- these parameters were determined by a fit of equation (3) to the measured cross section (table 1).

The good agreement between the experimental cross section and the Pattard formula for DPI supports the interpretation, that the measured triple-detachment cross section to a large part is due to simultaneous removal of a $1s$ and a $2p$ electron by a single photon. The result of the subsequent (Auger) deexcitation cascade is independent of the photon energy and the measured cross section shape is thus determined by the initial DPI process. It should be appreciated, that the $1s + 2p$ DPI cross section of F^- could be measured over an extended energy range including the cross-section maximum. This by far exceeds what has been achieved in earlier measurements of photodouble detachment of negative ions, which were restricted to just a few hundred meV near the associated threshold [69–71]. As compared to photoabsorption measurements in gases, where a weak signature of the $1s + 2p$ DPI has been observed for neutral neon [72], the merged-beams technique by its sensitivity for the charge state of the product-ion allows for a disentanglement of the contributions from direct single and double photodetachment processes.

For C^- the measurements could be extended to even beyond the threshold for double K -hole creation [28] (figure 5). A prominent feature in the cross-section σ_5 for net five-fold detachment is associated with $1s + 1s$ DPI visible at photon energies beyond approximately 700 eV. Moreover, this feature follows the photon-energy dependence of equation (3). In addition, this cross section exhibits a signature of $1s + 2s$ DPI as well. These processes cannot be observed in the other product channels where they are masked by competing processes including the creation of a hole with simultaneous excitation of a valence electron and their subsequent autoionization.

A rough estimate for the ratio of double-to-single K -hole production can be inferred from the magnitudes of the cross

section for net double and fivefold detachment. This ratio amounts to about 1% and agrees well with the ratio of 0.3%, that was measured for $1s$ and $1s + 1s$ inner-shell photoionisation of neon, and the theoretical prediction to increase with decreasing nuclear charge [73]. The determination of a more accurate value from the C^- data require a better knowledge of the various deexcitation rates and the formation of the various product charge states, than what is currently at hand. It is interesting to note that the ratio of double vs single core-hole production is much larger in atoms and atomic anions as compared to molecules. For carbon-containing molecules this ratio was found to be typically only 0.1% [74]. At present, there is no explanation for this difference.

4. Theoretical developments

The experimental findings summarized above challenge atomic structure theory in several ways. Difficulties arise especially from (1) the coupling of the inner-shell core holes to the valence shells, (2) the strong correlations that govern the dynamics of atomic anions and (3) the complexity and depths of the deexcitation cascades. In particular, the issues (1) and (3) require a considerable extension of the theoretical methods as compared to the computational tools that are applied to outer-shell photodetachment.

Gorczyca [8] has reviewed early theoretical work on inner-shell photodetachment of Li^- , B^- , and C^- focussing particularly on the near K -threshold resonances which are discussed in section 3.1. An accurate description of these resonances already required to incorporate the post-collision interaction (PCI) into the formalism in order to describe the K -shell detachment. Indeed, PCI (may) result in the recapture of the initially emitted photoelectron following the Auger decay of the K -hole (see also [75]) and may significantly reduce the theoretical resonance strength for Li^- leading to an excellent agreement with the experimental values. For C^- , in contrast, it was found that PCI does not have a significant effect and good agreement with the experiment available at the time of Gorczyca’s review was already obtained with more traditional coupled-channel approaches for the calculation of photoabsorption.

For light ions, inner-shell photodetachment primarily leads to the production of singly charged positive ions. For example, the strength of the $C^-(1s2s^22p^44P)$ resonance is dominated by the contribution of the net-double-detachment channel (figure 2) making up for about 90% of the total absorption. Thus, the contribution of the triple-detachment channel is smaller than the systematic uncertainty of the experimental cross-section scale (cf section 2). Therefore, the theoretical cross sections [8] for photoabsorption were rightfully expected to compare well with the measured cross section for net double detachment. However, these expectations do not apply for higher-photon energies (figure 5) and for atomic systems with more electrons where broad distributions of product-ion charge states result from inner-shell ionisation. For such atomic systems, large-scale calculations of Auger cascades are required for predicting the correct charge-state distributions [76, 77].

In the present context, systematically enlarged multiconfiguration Dirac-Fock *ab initio* calculations have been performed for resonant inner-shell photodetachment of O^- [9]. These computations showed that the calculated resonance width and branching fractions for double and triple detachment only agree with the experimental findings if double shakeup (and shakedown) of the valence electrons and the rearrangement of the electron density in the course of the autoionisation are taken into account [78, 79]. These higher-order multi-electron processes are manifestations of the inner-shell and intra-shell correlation effects that govern the inner-shell photodetachment dynamics of most atomic anions.

A particular challenge for atomic theory is DPI and, in general, all processes with two electrons in the continuum. These processes rigorously require to construct scattering states with two outgoing (continuum) electrons. In section 3.3, therefore, the experimental cross sections are compared with a semi-empirical scaling formula, since quantum theoretical results are not available. A step forward in this direction has been made very recently by Kheifets [80] who derived the correct shape of the $1s + 2p$ DPI cross section for F^- from perturbative and coupled-channel treatments of electron-impact ionisation. The calculations for DPI of C^- [28] revealed that the double removal of both K -shell electrons by a single photon is accompanied, in addition, by shake processes which make the theoretical treatment even more demanding.

Despite the extraordinary scale of the above mentioned computations significant differences, e.g., between theoretical and experimental absolute cross sections still remain [9, 12, 80]. For example, a full theoretical description of the rich C^- resonance structure discovered by Perry-Sassmannshausen *et al* [28] (figure 2) is well beyond current reach. Further efforts and improvements of state-of-the-art atomic theory are therefore required, although some major developments in this direction are already under way [81].

5. Conclusions and outlook

Experimental developments in synchrotron-radiation and ion-beam technologies of the past decade have led into a new era of inner-shell photoionisation studies with ionised small quantum systems. As discussed above, the recent experimental results for inner-shell detachment of atomic anions bear vivid witness of this development. The high photon flux at the PETRA III beamline P04 as well as the excellent product-ion selectivity of the photon-ion merged-beams end-station PIPE allows one to measure extremely small atomic cross sections in the kilobarn range. This facilitates the observation and quantitative measurement of rare atomic processes such as the simultaneous removal of two inner-shell electrons by a single photon.

The available photon energy range at PETRA III beamline P04 permits the investigation of single and double K -shell photodetachment of heavier ions up to Cl^- and Na^- , respectively. Photodetachment measurements with Si^- have already been performed and are currently being analysed. Further steps towards enlarging the experimental data base on inner-shell processes in atomic anions are planned. This will also stimulate further development of the theoretical methods and might

eventually lead to a better understanding of the correlated dynamics in these fundamental atomic systems.

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