Ion charge-resolved branching in decay of inner shell holes in Xe up to 1200eV

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Abstract
Using a new multi-electron multi-ion coincidence apparatus and soft x-ray synchrotron radiation we have determined branching ratios to final Xe\(^{n+}\) states with \(2 < n < 9\) from the 4d\(^{-1}\), 4p\(^{-1}\), 4s\(^{-1}\), 3d\(^{-1}\) and 3p\(^{-1}\) Xe\(^{2+}\) hole states. The coincident electron spectra give information on the Auger cascade pathways. We show that by judicious choice of coincident electrons, almost pure single charge states of the final ions can be selected.

Keywords: inner shell holes, multiple Auger decay, branching ratios, coincidence detection

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

Introduction

Although Xe is indeed a well-studied showcase for atomic inner shell ionization as pointed out by Becker et al [1], the ultimate fates of states with inner shell holes deeper than the outermost ones, 4d\(^{-1}\) and 4p\(^{-1}\) still deserve more detailed study. Here we introduce a new electron–ion coincidence apparatus and use it to measure the final charge distributions directly for all initial pure single hole states up to the 3p\(^{-1}\) levels. We also show that by selection of the number and energies of coincidently detected electrons we can select formation of almost pure single charge states. This ability, when carried over to molecules, will allow systematic study of the effect of the charge state on the dynamics of dissociation by the so-called Coulomb explosions. The primary objective of this work is to provide a reliable prototype for such studies on molecules containing iodine atoms. In line with this physico-chemical orientation of the work we use the nl nomenclature for orbitals instead of the KLMN terminology traditionally used in Auger spectroscopy.

Important previous studies of Xe inner shell processes include the ion yield measurements as a function of photon energy [2–4] and the electron–ion coincidence measurements of Luhmann et al [5]. Much detailed insight is given by the electron–electron coincidence measurements of Hikosaka et al [6, 7] and the threshold electron–ion coincidence work of Matsui et al [8]. High resolution Auger electron spectra have been acquired and analysed in detail after 4d \([9, 10]\] and 3d \([11, 12]\) inner shell hole creation, and interpreted with some identification of the Auger cascades and final ion states, and with theoretical calculation of the rates of the transitions involved. Hartree–Fock calculations of the branching from single hole states have been done by Kochur et al [13] including all the significant branching pathways. Most recently a new Monte-Carlo method for efficient calculation of the branching in these processes has been developed by Son and Santra [14] and has been applied to the inner shell ionization of Xe at the high fluences available from an x-ray free-electron laser.

The majority of previous measurements of the branching from inner shell hole states to different charge states of Xe \([2–4, 15]\) have operated on the principle of measuring the yields of Xe\(^{n+}\) ions as a function of the soft x-ray energy and observing the steps in yield at each edge. Because of the complexity of the processes that can be induced by x-ray absorption, this method has limitations. In the energy region some eV below a true edge, resonant processes in which an electron is promoted from an inner shell to a normally unoccupied orbital often have large excitation cross-sections and can decay to very different ionized
The basic scheme of the apparatus is illustrated in figure 1 which presents a new, third version of a multi-electron–ion coincidence setup based on a magnetic bottle spectrometer (see [18, 19] and references therein). Monochromatic light from beam line U49/2 of the BESSY-II storage ring operated in single bunch mode arrives in sub-ns packets at a repetition rate of 1.25 MHz. To be useful for our experiments this rate is reduced to 10 kHz by a synchronous chopper [20]. The light then intersects a narrow jet of target gas within both the divergent magnetic field of a conical permanent magnet and a cylindrically symmetrical electrode array which forms a perpendicular mass spectrometer designed for velocity map imaging (VMI) [21]. In the present application, imaging was not used but mass to charge ratios were determined from the ions’ time of flight. Because the strong magnetic field in the interaction region has an undesired effect on the ion trajectories, external magnets are mounted after a short distance along the ion flight path to compensate. Their effect is to centre ions of all mass-to-charge ratios effectively on the detector, though the centres for light ions, particularly H$^+$, are still slightly displaced. The electrons are funnelled by the field of the magnet into a long (2 m) solenoid which guides them to the distant detector, where their flight times, relative to the light pulse, are measured. Because the electric fields needed to extract ions would fatally destroy the electron energy detection, the fields are pulsed a few 10 s of ns after the light pulses, leaving time for the electrons to enter the field-free flight tube (beyond a first grid) before the pulses are applied. The arrival times of electrons and ions are recorded by multi-hit timing electronic systems, allowing any number of electrons and ions to be detected in coincidence provided they do not arrive at the same time (electrons) or at the same time and in the same position (ions). The configuration of magnetic fields constitutes a magnetic bottle [22], which ensures that almost all electrons formed at the intersection of light and target gas are guided to the detector. The total collection-detection efficiency for electrons is therefore determined largely by the detector, which comprises a Z-stack microchannel plate configuration. The actual efficiency is easy to determine absolutely in pure single ionization since the rates of true
electron–ion coincidences $C_{\text{ie}}$ and the rate of ion detection $E$ are given by:

$$C_{\text{ie}} = N f_{\text{e}} : E = N f_{\text{f}} ,$$

where $N$ is the number of ionization events, $f_{\text{e}}$ is the total efficiency of ion detection and $f_{\text{f}}$ is the same quantity for electrons. The quotient of these two measured rates, $C_{\text{ie}}/E$ is equal to the electron efficiency. This scheme can be extended to multiple ionization since the rate of coincidences of an atomic ion carrying $n$ charges with $n$ detected electrons is $N f_{\text{e}}^{n}$, while the coincidence rate where only $n-1$ electrons are detected is $N f_{\text{e}}^{n-1}(1 - f_{\text{e}})$. The measured ratio of these is $f_{\text{e}}/(1-f_{\text{e}})$ from which $f_{\text{e}}$ is readily derived. The total detection efficiency in these experiments was found by these methods to be 62 ± 3%, independent of energy over the range up to at least 250 eV.

Because we aim to determine the relative yields of ions in different charge states, the collection/detection efficiency for the ions is of great importance. For technical reasons, the potential of the front face of the MCP detector, which determines the energy of the ions at impact, was kept at −2350 V, which is too low to allow all Xe$^{n+}$ ions to be detected with equal efficiency [2, 5, 23]. For some charge states the ion efficiency can be determined absolutely in the same way as for electrons, by comparing the coincidence rate with the corresponding electron rate. This works if an electron energy range can be selected where only a single ion charge state is formed in coincidence, for instance valence electrons for single ionization and isolated Auger electrons for double ionization. The relative ion efficiencies can be determined independently by comparing measured overall mass spectra at particular photon energies with reference spectra. We used the spectra of Saito and Suzuki [2] and Holland et al [24] for Xe and those of Tamenori et al [25] for Kr, which was examined as a consistency check. The relative values were used to extend our absolutely determined ion efficiencies to the more highly charged ions. The efficiencies were found to be uniformly 50 ± 5% for Xe ions with six or more charges, but less for the less highly charged ions down to only 8 ± 2% for Xe$^{2+}$. A check of the final values was carried out by comparison of our results with the specific branching ratios from the 4d$^{-1}$ hole states of Xe (below) determined by Luhmann et al [5], which are in excellent agreement.

**Results and discussion**

**Ionization from different shells**

4σ$^{-1}$. The decay of the 4d$^{-1}$ hole state of Xe has been very extensively studied. The branching between single and double Auger decay was measured by Kaemerling et al [26] and more precisely by Luhmann et al [5], who determined the fraction of double Auger decay from the whole 2D state forming Xe$^{3+}$ as 18.8(9)% with negligible formation of Xe$^{4+}$ by optical emission. Our result for the same quantity is 17.4 ± 1%, where the error is not statistical but arises from uncertainty in the relative collection efficiencies for the low-charge ions. The two components of 2D behave slightly differently; for double Auger decay of 2D$_{5/2}$ we find 16.3 ± 1% of Xe$^{3+}$ (Luhmann et al, 16.6 ± 9%) while for 2D$_{3/2}$ our result is 20.5 ± 1% (Luhmann et al, 21.9 ± 9%). The calculations of Kochur et al [13] did not distinguish between the substrates and severely underestimate the proportion of double Auger as 0.3% compared with the 16% observed. It seems that the calculations did not include all the actual pathways, including the coherent ones, revealed in electron–electron correlation maps [28]. The more recent calculations of Luhmann et al [5] also underestimate the same quantity as 7% or 8%. The intensities of final states formed in the single Auger decay from the 4d$^{-1}$ hole states were measured by Eland et al [27] and those formed in double decay were identified with their branching ratios by Penent et al [28, 29], Penent et al also showed that the double Auger decay is to a considerable extent (ca 33%) indirect, going through superexcited states of Xe$^{2+}$ which subsequently autoionise. Such indirect processes or Auger cascades are very common if not the majority processes for most inner shells. When the photon energy is close to an inner shell edge, complex electron correlation phenomena generally called post collision interaction(PCI) occur; these have been studied in detail at the Xe 4d edge by Scheinerman et al [30].

The ‘4p$^{-1}$’ appellation conceals the fact that there is no single hole state here; the underlying state is so strongly mixed with 4d$^{-2}$nf and 4d$^{-2}$ef configurations that no sign of the $J = 1/2$ component is seen in the electron spectrum and the $J = 3/2$ peak is split into several subpeaks. The decay of this group of states has been investigated by the threshold electron–ion coincidence method [31], by Auger spectroscopy [32, 33] and by multielectron coincidence [6]. From these works it is already known that the main products are Xe$^{3+}$ and Xe$^{4+}$ arising through complex Coster–Kronig Auger cascades. According to the results of threshold electron–ion coincidence [31] the formation of Xe$^{3+}$ is 34% of the total decay of the ‘4p$^{-1}$’ hole, while Hikosaka et al [6] put it at only 9% from multi-electron coincidence. Our measurements do not agree with the latter estimate, but point out that the determination is very difficult because of the nature of the electron spectra. Electron spectra, taken in coincidence with the Xe$^{3+}$ ion at 180 and 250 eV photon energy, show a clear 4p signal as a peak with a flat, level background before and after the peak. In coincidence with Xe$^{4+}$, by contrast, the ‘4p’ peak has a very strong shoulder to lower electron energy (higher binding energy) which makes it almost impossible to separate out the contribution of the peak itself. A raised background level below the peak is seen in the total electron spectra measured at both energies, and also in figure 1(a) of Hikosaka et al [6]. Because no Auger electrons arising from 4d$^{-1}$ ionization can appear in coincidence with Xe$^{4+}$, only Auger electrons from 4p itself, or (at 250 eV) from 4s$^{-1}$ could possibly contribute. The 4s ionization is exceedingly weak, and the only Auger decay from 4p giving Auger electrons of the necessary energy would lead to Xe$^{9+}$ formation, whose measured intensity is negligible. We therefore conclude that
the interfering intensity at binding energies just above 4p arises from 4p satellites. By extracting pure peak intensities from the electron–ion coincidence spectra as best we can, we find the following decay proportions from the part of the electron spectrum most closely resembling 4p−1: Xe3+; 3 ± 1.5%, Xe4+; 62 ± 3%, Xe5+; 35 ± 7%. This result agrees best with the ratios from threshold electron–ion coincidence [11]. The calculations of Kochur et al. [13] agree with the experimental values to the extent that Xe4+ is the most abundant; the fraction of the higher charge state, Xe5+, is again severely underestimated as 5.1%.

Because Hikosaka et al. [6] and Partanen et al. [34] have examined the electron–electron correlations connected with 4p−1 decay in detail, we refrain from elaborating on them here. Suffice it to confirm that the Auger electrons of about 55 eV energy forming 4d−5p−1 essentially all end up as Xe5+, while the group with about 32 eV all go to Xe4+, as indicated in [23]. Our spectra seem at first sight to be inconsistent with Hikosaka et al. on one other point: the threshold for formation of Xe4+ at both 180 and 250 eV photon energy is seen in our data as 111 ± 2 eV, which is not compatible with their value of 106.3 eV. The lower value agrees with the sum of standard ionization energies from data tables [35]. We therefore suspect that lowest level of Xe4+ is not formed in high abundance by the Auger cascade pathways that we observe.

4s. The cross section for populating the 4s−1 level is small, and the photoline shows in the electron spectrum at 250 eV photon energy as a weak peak on a strong background. Only when the electron spectrum is examined in coincidence with Xe5+ does the 4s−1 photoline stand out as the main distinct feature on a relatively smooth background. This is certainly because the ground state of Xe5+ lies at about 170 eV, well above 4p and all other outer shells, so apart from formation of 4s−1, the first step of any other indirect pathway to it must involve multi-electron transitions. Estimating the background contribution is again the major uncertainty in determination of the branching ratios from 4s−1; our estimates are: Xe3+; 34 ± 10%, Xe4+; 35 ± 8%, Xe5+; 30 ± 5%. The calculations of Kochur et al. [13] differ substantially, giving 16.5%, 77.4% and 5.1% for the same ions. The only previous experimental investigation of the decay pathways from this initial state has been the multi-electron coincidence work of Hikosaka et al. [7], whose spectra show that it decays at least in part by a Super Coster–Kronig transition to selected 4d−2 double hole states. These states decay predominantly to Xe5+, as discussed below. The ion–electron coincidence spectrum shows that while some Xe5+ is formed at 250 eV photon energy through 4s−1, the majority is formed by other mechanisms, as the electron peak for 4s−1 in this channel has less than 1/15 of the intensity of the background, which itself extends right down to the onset of Xe4+ at 170 eV. If Xe3+ is formed through 4s−1 there are just four more electrons to add to the spectrum and all must have energies less than about 40 eV.

3d. Decay of the 3d−1 hole states at 676 and 689 eV binding energy is seen in the high resolution M4s–NN Auger spectrum [9], later analysed in detail by Jonauskas et al. [12] and in the ion yield measurements of Matsui et al. [8] and Partanen, Sankari et al. [11]. The Auger transitions from this hole state leave Xe species with enough energy to be ionized at least up to ninefold. The present mass spectra coincide with the individual spin–orbit levels show no measurable difference between 2D3/2 and 2D5/2 in branching towards the different ion states. We obtain Xe3+; 4.7 ± 2%, Xe4+; 53.7 ± 1%, Xe5+; 25.6 ± 1%, Xe6+; 13.0 ± 0.5%, Xe7+; 2.4 ± 0.3%, Xe8+; 0.4 ± 0.2%. These values are close to, but not in perfect agreement with those of Partanen, Sankari et al. [11] and to those of Matsui et al. [8]. In this case the theoretical estimates of Kochur et al. [13] for the same ions are quite good agreement with our experimental values, at 5%, 46.0%, 31.8%, 15%, 2.1% and 0.1%. The strongest peak in the Auger electron spectra is found at about 520 eV, and is identified with the Auger transitions from 3d−1 to 4d−2, that is, creating a double hole in the 4d shell. Our electron–ion coincidence spectra show that the final states populated from the whole range of 4d−2 levels as created in this way are Xe4+, 83% and Xe5+, 17%. The creation and decay of the states formed with this double hole have been examined in great detail using multi-electron coincidence by Hikosaka et al. [7], after their formation by double photonization at 301.6 eV. This is not the main channel to Xe5+, however, as our spectra show that this ion is formed mainly by population from 3d−1 via states with 4d−14p−1 and 4d−14s−1 configurations. The present coincidence data are illustrated by threefold coincidences in figure 2, which shows electron spectra coincident with both Xe5+ ions and photoelectrons from formation of Xe 3d−1(2D3/2,2). The scale at the top of the figure is the binding energy of Xe5+ states created by the initial Auger transition from 3d−1, while the scale at the bottom is the measured electron energy. Minimum energies for appearance of the different charge states are indicated on the figure; the position of the Xe5+ threshold relative to the 4d−2 peak shows that both of the final two Auger electron emitted in formation of Xe5+ by this route are of low energy, less than 50 eV. Details of those low energy electrons are seen in the coincidence measurements of Hikosaka et al. [7], but here they are obscured by overlap with the 3d−1 electron peaks. The major process of Xe5+ formation, goes via 4p−14d−1; here the three later Auger electrons share 40–80 eV between them. In the subsidiary process where Xe5+ is formed from 3d−1 via 4s−14p−1, one of the cascade Auger electrons has about 110 eV energy and is clearly seen as an additional peak in the spectrum (and also in complementary coincidence maps). If the 110 eV electron is the third one in this route (3d−1 Xe5+(676 eV) → 4s−14p−1 Xe3+;[306 eV] → Xe3+(ca 196 eV) → Xe2+; 162 eV) the last two electrons are again of low energy. Formation of Xe6+ also goes through 4s−14p−1 as the major route, and through a state of Xe5+ near 360 eV which could be 4s−2. In formation of the higher charge states, Xe7+ and Xe8+, the electron spectra show little structure and even the 3d−1 lines do not stand out strongly from a continuous background, as also reported by Matsui et al. [8].

3p. The decay of the 3p−1 states was examined by means of ion yield measurements by Saito and Suzuki [2, 36] and in the
early estimates by Carlson et al.\[37\]. The 2P3/2 and 2P1/2 levels at 941 and 1002 eV are clearly visible at 1200 eV photon energy, but with a non-statistical relative intensity ratio of 5:1. The decay patterns from the two levels are detectably different:

\[
\begin{array}{cccc}
4+ & 5+ & 6+ \\
\hline
3P3/2 & 3 \pm .8 & 16.8 \pm .8 & 28.3 \pm 2 \\
2P1/2 & 3.2 \pm 1.5 & 9.1 \pm 2.2 & 27.2 \pm 3.3 \\
7+ & 8+ & 9+ \\
38.6 \pm 2 & 11.5 \pm 1.5 & 1.7 \pm .6% \\
39.6 \pm 3.6 & 16.4 \pm 2.4 & 4.5 \pm 1% \\
\end{array}
\]

The overall pattern predicted by the theoretical calculations of Kochur et al [13] is in fair agreement with these figures, as is the prediction of a difference between 2P3/2 and 2P1/2, but there are differences of detail and the abundance of the highest charge states is underestimated. The higher yields

![Figure 2](image-url)  
**Figure 2.** Spectra of electrons coincident with both an electron from 3d−1(2D5/2) ionization and the indicated Xe^m+ ions at 710 eV photon energy. The lowest energy part is cut off because electrons from many processes pile up there, including the 3d ionizations themselves. At the high electron energies, the energy scale should be read as indicative rather than exact, because the calibration is less reliable in this region. The strong peak coincident with Xe^4+ comes from intermediate formation of Xe^2+(4d−2) as discussed in the text. Intermediate ionizations involved in formation of the other ions are indicated.

![Figure 3](image-url)  
**Figure 3.** Mass spectra coincident with selected numbers and energies of electrons. For Xe^2+, Auger electrons of around 33 eV are selected at 110 eV photon energy. For Xe^3+, three electrons with summed energy between the estimated appearance energy of the ion and the ion of next higher charge are chosen. For Xe^4+, we take electrons in the main Auger peak at 550 eV in coincidence with 3d5/2 ionization at 710 eV. For Xe^5+ at 710 eV, four electrons with energy sum between 475 and 535 eV are taken and finally for Xe^6+ we select one electron between 300 and 350 eV together with the 3d5/2 photoline.

![Figure 4](image-url)  
**Figure 4.** Graphical representation of the branching to different charge states of Xe from individual shells as lines of different thickness with very low intensity as dashed lines. Subshells are not distinguished and only the minimum energy for production of each charge is shown. For charge states higher than 5+ the energies marked are theoretical estimates \[38\] as exact experimental values are not available.
of Xe\(^{8+}\) and Xe\(^{9+}\) from \(^2\)P\(_{3/2}\) seem unlikely to be explicable simply from their energies relative to the thresholds for forming the two ions, which must be near 430 and 606 eV respectively [35] and thus well below the 3p\(^{-1}\) levels. Unfortunately our electron spectra at the energies where 3p\(^{-1}\) levels are formed do not have good enough statistics to allow us to deduce detailed decay pathways. The Coster–Kronig transition 3p\(^{-1}\) → 3d\(^{-2}\), which would otherwise be favoured, is energetically forbidden. There is a clear peak at about 180 eV in the electron spectrum coincident with ions and the \(^2\)P\(_{3/2}\) photoline, suggesting that the transition 3p\(^{-1}\) → 3d\(^{-1}\)4d\(^{-1}\) plays a role as a first step in the cascades leading to the more highly charged ions. (We estimate the energy of the 3d\(^{-1}\)4d\(^{-1}\) states by adding the individual orbital binding energies to an estimated Coulomb repulsion term as 680 + 68 + 10 = 758 eV so the expected Auger energy is 941−758 = 183 eV.)

**Figure 5.** Comparison of the branching fractions predicted by the Hartree–Fock calculations of Kochur et al [13] with our measured branching fractions. The vertical scales show the common logarithm of the experimental fraction divided by the calculated one.

**Selection of individual charge states**

By selection based on the presence of coincident electrons in the right numbers and of the appropriate energies, it should ideally be possible to choose any individual degree of ionization. In practice this is easy for relatively low charge states, but more difficult for higher ones. Part of the difficulty is purely technical and hopefully temporary; our present electronics do not register electrons separately when they arrive close together in time, so some electrons are missed, particularly at high energies where arrival times bunch together. Furthermore, even with high collection efficiency \(f_e\) for individual electrons, the overall efficiency for \(n\) electrons, \(f_e^n\), becomes very small when \(n\) is high. For the higher charges we cannot therefore isolate \(n\)-fold ionization by requiring detection of \(n\) electrons of the correct energy sum. Instead we try to choose particular electrons which identify cascades leading to the desired final state. The present degree of success is illustrated in figure 3 where the less perfect selection of the higher charges is evident.

**Conclusions**

In this work we have commissioned new apparatus capable of detecting multiple electrons and ions in coincidence, with good resolution for both ion mass and electron energy. By using it we have measured the branching patterns to final charge states of Xe from pure inner-shell hole states from the 4d to the 3p shells, with resolution of the spin–orbit substates. The branching is illustrated graphically in figure 4 in relation to the minimum energy for production of each final charge on the Xe atom, showing that the highest energetically accessible charge is reached from the shallower inner shell holes, but not from 3d or 3p. We believe that these are the most comprehensive and reliable data available on these quantities, and provide both a challenge to theory and a guide for future experiments. Comparison of the branching fractions with those predicted by rather comprehensive Hartree–Fock calculations [13] is made graphically in figure 5, which shows that the calculations make accurate predictions for all but the highest charges. The proportion of the highest charge states is severely underestimated in every single case. Higher level calculations are scare, but those we are aware of still underestimate the formation of the most highly charged ions.

**Table 1.** Percentage branching to Xe\(^{n+}\) ion states after hole creation in inner shells.

|        | 4d\(_{5/2}\) | 4d\(_{3/2}\) | '4p' | 4s | 3d | 3p\(_{3/2}\) | 3p\(_{1/2}\) |
|--------|-------------|-------------|-----|---|----|-------------|-------------|
| Xe\(^{2+}\) | 83.7 ± 1 | 79.5 ± 1 | 3 ± 1.5 |
| Xe\(^{3+}\) | 16.3 ± 1 | 20.5 ± 1 | 62 ± 3 |
| Xe\(^{4+}\) | 35 ± 7 | 35 ± 8 | 53.7 ± 1 | 3 ± 8 | 3.2 ± 1.5 |
| Xe\(^{5+}\) | 30 ± 5 | 25.6 ± 1 | 16.8 ± 8 | 9.1 ± 2.2 |
| Xe\(^{6+}\) | 13 ± .5 | 28.3 ± 2 | 27.2 ± 3.3 |
| Xe\(^{7+}\) | 2.4 ± .3 | 38.6 ± 3.6 | 39.6 ± 3.6 |
| Xe\(^{8+}\) | 0.4 ± .2 | 11.5 ± 1.5 | 16.4 ± 2.4 |
| Xe\(^{9+}\) | 1.7 ± .6 | 4.5 ± 1 |
though less severely. It seems likely that to accurately represent the multi-electron as well as multi-step processes involved, inclusion of electron correlation must be necessary in addition to some relativistic corrections. None of the extant calculations include coherent 2-electron double Auger processes, which are certainly significant in addition to stepwise pathways, particularly for the 4d shell, as demonstrated by electron–electron correlations [28]. For the deeper inner shell holes, where Coster–Kronig transitions are dominant, coherent two-electron decay is less significant, but still contributes particularly to formation of the most highly charged ions.

The branching patterns to final charges states of Xe, as measured in this work and collected in table 1, are a prototype for creation of highly charged molecules by inner shell ionization. Several of these, an additional step, possible at all stages of the Auger cascades, will be intramolecular charge transfer. Timing experiments with femtosecond resolution will be needed to characterise the charge evolution in detail and its likely competition with nuclear motion. By selecting the ejected electrons by number and energy, we have shown that predominantly single charge states can potentially be selected; the ability to do this for molecular ionization will be a great asset in a forthcoming systematic study of the dynamics of Coulomb explosions.

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References

[1] Becker U et al 1989 Phys. Rev. A 39 3902
[2] Saito N and Suzuki I H 1992 Int. J. Mass Spectrom. Ion Process. 115 157
[3] Tawara H et al 1992 J. Phys. B: At. Mol. Opt. Phys. 25 1467
[4] Tonuma T et al 1987 J. Phys. B: At. Mol. Phys. 20 L31
[5] Luhmann T et al 1998 Phys. Rev. A 57 282
[6] Hikosaka Y et al 2007 Phys. Rev. A 76 032708
[7] Hikosaka Y et al 2007 Phys. Rev. Lett. 98 183002
[8] Matsui T et al 2004 J. Phys. B: At. Mol. Opt. Phys. 37 3745
[9] Werne L O, Bergmark T and Siegbahn K 1972 Phys. Scr. 6 141
[10] Partanen L et al 2006 J. Phys. B: At. Mol. Opt. Phys. 39 4515
[11] Partanen L et al 2005 J. Phys. B: At. Mol. Opt. Phys. 38 1881
[12] Jonauskas V et al 2003 J. Phys. B: At. Mol. Opt. Phys. 36 4403
[13] Kochur A G et al 1994 J. Phys. B: At. Mol. Opt. Phys. 27 1709
[14] Eland J H D and Feifel R 2006 Chem. Phys. 327 85
[15] Samson J A R and Haddad G N 1974 Phys. Rev. Lett. 33 875
[16] Kikas A et al 1996 J. Electron Spectrosc. Relat. Phenom. 77 241
[17] Alitalo S et al 2001 J. Electron Spectrosc. Relat. Phenom. 114-116 141
[18] Feifel R, Eland J H D, Storchi L and Tarantelli F 2006 J. Chem. Phys. 125 194318
[19] Eland J H D, Linusson P, Mucke M and Feifel R 2012 Chem. Phys. Lett. 548 90
[20] Plogmaker S et al 2012 Rev. Sci. Instrum. 83 031115
[21] Eppink A T J B and Parker D H 1997 Rev. Sci. Instrum. 68 3477
[22] Kruit P and Read F H 1983 J. Phys. E: Sci. Instrum. 16 313
[23] Hayaishi T et al 1984 J. Phys. B: At. Mol. Phys. 17 3511
[24] Holland D M P et al 1979 J. Phys. B: At. Mol. Phys. 12 2465
[25] Tamenori Y et al 2004 J. Phys. B: At. Mol. Opt. Phys. 37 117
[26] Kaemmerling B et al 1992 J. Phys. B: At. Mol. Opt. Phys. 25 3621
[27] Eland J H D et al 2003 Phys. Rev. Lett. 90 053003
[28] Penent F et al 2005 Phys. Rev. Lett. 95 083002
[29] Penent F et al 2005 J. Electron Spectrosc. Relat. Phenom. 144 7
[30] Scheinerman S et al 2006 J. Phys. B: At. Mol. Opt. Phys. 39 1017
[31] Hayaishi T et al 2002 J. Phys. B: At. Mol. Opt. Phys. 35 141
[32] Heinaesmaeki S et al 2004 J. Electron Spectrosc. Relat. Phenom. 137–140 281
[33] Kivimaeki A et al 1998 J. Electron Spectrosc. Relat. Phenom. 93 89
[34] Partanen L et al 2007 J. Phys. B: At. Mol. Opt. Phys. 40 4605
[35] Kramida A et al 2014 NIST Atomic Spectra Database version 5.2
[36] Saito N and Suzuki I H 1992 J. Phys. B: At. Mol. Opt. Phys. 25 1785
[37] Carlson T A, Hunt W E and Krause M O 1966 Phys. Rev. 151 41
[38] Borovik A 2010 Doctoral Thesis Justus-Liebig University, Giessen