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Valence shell direct double photodetachment in polyanions

Claire Brunet¹, Rodolphe Antoine¹, Philippe Dugourd¹, Denis Duflot², Francis Canon^{3,4}, Alexandre Giuliani^{3,5,6} and Laurent Nahon³

¹ Université Lyon 1-CNRS, Université de Lyon, 69622 Villeurbanne cedex; UMR5306, Institut Lumière Matière, Villeurbanne, France

² Université Lille 1, Sciences et Technologies Laboratoire de Physique des Lasers, Atomes et Molécules UMR CNRS 8523 Bâtiment P5, F-59655 Villeneuve d'Ascq Cedex, France

³ SOLEIL, l'Orme des Merisiers, St Aubin, BP48, F-91192 Gif sur Yvette Cedex, France

⁴ INRA, UMR1324 Centre des Sciences du Goût et de l'Alimentation, F-21000 Dijon, France

⁵ INRA, UAR1008, CEPIA, Rue de la Géraudière, BP 71627, F-44316 Nantes, France

E-mail: giuliani@synchrotron-soleil.fr

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Abstract. A valence shell study of electrosprayed insulin protein polyanion photodetachment was carried out on a vacuum ultra-violet synchrotron radiation beamline coupled to a radiofrequency ion trap, for both close- and open-shell species. A two-electron photodetachment is observed, which arises from two different mechanisms that are disentangled: a sequential multi-photon absorption and a direct one-photon two-electron process. The threshold for the direct double-electron ejection is measured at 11.4 eV and corresponds to electronic excitation in the valence shell, which makes it the first observation of direct double photodetachment in the valence shell. The results are discussed in

⁶ Author to whom any correspondence should be addressed.



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the light of previous knowledge from multiple photoionization and *ab initio* calculations on model polyanions. Double photodetachment appears to be a relaxation mechanism that leads to oxidized anions of striking stability, a feature of high relevance in radiobiology.

The observation of multiply charged species was first reported by Thomson about a century ago [1]. Already at that time the mechanism of formation of these species was being questioned. Ions appearing at one-half the mass-to-charge ratio of the parent atomic or molecular ions in conventional mass spectrometry were correctly identified as doubly charged ions, although usually the relative abundances of these ions are low. Soon after these pioneering studies, a few electron impact studies in rare gases appeared, with appearance energy determination [2]. It was not until 1971 that photons in the x-ray regime were employed to doubly ionize atoms [3]. The interest in di-cations arose from potential applications of the large amount of energy stored in these systems, from theoretical interest [4–6] and from their particular reactivity, which has been suggested to play an important role in planetary ionospheres [7–9].

Different mechanisms may be distinguished to account for electron double emission [5, 10, 11]. First, direct double valence ionization following single-photon absorption might happen, an effect due to electron correlations, which therefore cannot be described within independent electron models. The ‘knock-out’ inelastic model [12, 13] appears to account very well for this direct non-local process even in quite large organic molecules [14]. Doubly charged species may also be produced following inner-shell excitation/ionization, in which case the primary excited monocation relaxes through the Auger effect by emission of a second electron, leading to a doubly charged cation. Finally, two electrons may be emitted sequentially by two independent interactions of the precursor ion with incident light in a sequential mechanism involving linear or nonlinear photon-induced processes.

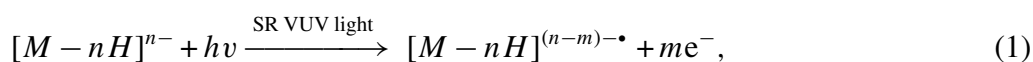
The valence electrons in anions experience very different potential energies than in neutral molecules and cations. In particular, an electron in the valence regions of a mono-anion experiences no net Coulomb attraction in its asymptotic regions, while corresponding electrons in cations and neutral molecules do experience such $-1/r$ attractions [15]. On the other hand, double detachment from a mono-anion would also induce Coulomb attraction. Inner-shell double photodetachment (DPD) has been reported independently by two pioneering groups for Li^- [16, 17] using merged beam techniques at synchrotron radiation facilities. The measurements were based on production of Li^+ , mainly occurring from $1s$ ejection followed by Auger decay. These pioneering studies have triggered experimental and theoretical studies in this new field of inner-shell photodetachment on negatively charged atoms and clusters [17–20]. To our knowledge, the only measurements of DPD on molecular anions concern an inner-valence DPD study of CN^- , in the 25–90 eV energy range, for which the main relaxation mechanism has been identified as inner-valence autoionization of excited CN^- leading to CN^+ [21] and of multiply charged C_{60} anions [22].

In the valence shell, photodetachment of atoms, molecules and clusters using visible and near-ultraviolet (UV) lasers has been an active and prolific field for decades [20, 23, 24]. Recently, developments relying on electrospray ionization have made possible the study of photodetachment spectroscopy for trapped biomolecular polyanions (proteins, peptides, nucleic acids, etc) using tunable UV lasers [25, 26]. For multiply charged anions, another situation arises, since a repulsive Coulomb potential is operative. This results in particular in the observation of anions with negative electron binding energies [27, 28]. For a particular

setup [29], double photodetachment has been observed [30] and attributed to a sequential mechanism involving multi-photon effects because of the non-linear ion yield with laser fluence.

In this paper, we report on the photodetachment spectroscopy of closed and open shell protein anions in the vacuum UV (VUV) up to 15.2 eV. We observe a double-electron detachment from the precursor ions in the valence shell region. We show that two mechanisms may account for the formation of the doubly photodetached ions: a sequential two-photon absorption and a direct one-photon two-electron mechanism. The measured threshold for the direct double-electron ejection at 11.4 eV corresponds to electronic excitation in the valence shell, which makes this observation the first report of direct double photodetachment in the valence shell.

This work is based on the concept of action spectroscopy of trapped ions in which photons from the VUV DESIRS beamline [31] at SOLEIL (France) are used as an activation method [32]. Monochromatic synchrotron radiation with 3 meV photon energy bandwidth (10^{11} – 10^{12} ph s $^{-1}$) is admitted inside a linear ion trap where the ions of interest are stored. The irradiation time is identical to the storage time and is controlled using a photon shutter with millisecond precision [33]. In order to ensure higher-order free radiation, upstream the monochromator a gas filter removes the high harmonics from the undulator [34]. After irradiation of selected anions, the mass spectrum is recorded, leading to the observation of charge reduced ions:



where $[M - nH]^{n-}$ stands for the multiply deprotonated anion formed by electrospray and $[M - nH]^{(n-m)-\bullet}$ is the photodetachment product, whose yield is monitored as a function of $h\nu$. Repeating this procedure over the photon energy range leads to the obtention of VUV action spectra. The experiments were performed on insulin, a small model protein consisting of 51 amino acids distributed in two chains linked together by two disulfide bridges.

The mass spectrum obtained after irradiation of the insulin 5-anion (m/z 1145.3) for 400 ms with 15 eV photons is shown in figure 1. The main photoproduct is the $[M - 5H]^{4-\bullet}$ anion (m/z 1431.6) resulting from single-electron photodetachment. This is in agreement with earlier reports on insulin polyanions in the near UV [35] and on VUV measurements on peptides [36, 37]. Another peak, detected at m/z 1909, is assigned to $[M - 5H]^{3-\bullet\bullet}$, which corresponds to a double loss of electrons from the $[M - 5H]^{5-}$ precursor. Normalization of the ion abundance to the photon flux and the total ionic current gives access to the partial relative cross section corresponding to the process at the origin of that ion, assuming a unitary form factor [38]. The partial relative cross section obtained for single photodetachment ($[M - 5H]^{4-\bullet}$ product ion) is presented in figure 2(a). The onset for single photodetachment observed in mass spectra for peptides and proteins has been reported at around 4 eV (309 nm) and corresponds to that of photoabsorption by the aromatic amino-acid residues [36]. In the VUV, spectroscopic studies on peptides have established that the photodetachment efficiencies show resonances, which could be assigned to particular electronic excitations [36, 37, 39, 40] followed by relaxation with emission of an electron. The feature observed here near 10 eV has already been observed for peptides [36, 37] and could correspond to high-excited states involving the peptide backbone. Figure 2(b) shows the partial relative cross section for the double photodetachment (the $[M - 5H]^{3-\bullet\bullet}$ ion). A clear onset is observed at $11.4 \text{ eV} \pm 0.1 \text{ eV}$ as derived from a threshold linear Wannier-type fitting [41]. The Wannier fitting is used here only as a convenient means of extracting the threshold value without physical assumptions of the underlying physics.

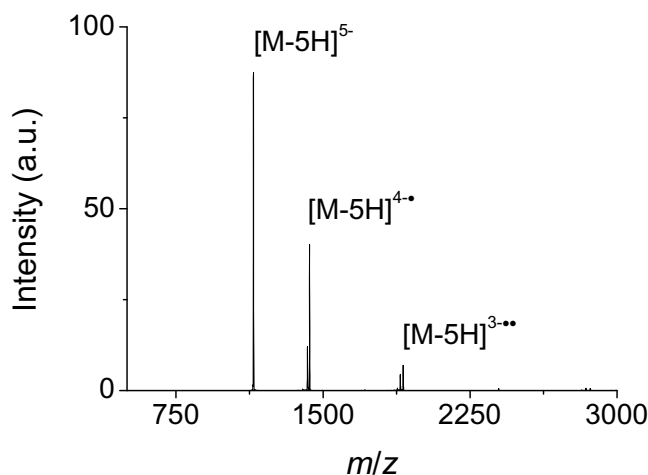


Figure 1. Mass spectrum after irradiation with 15 eV photons and 400 ms irradiation duration of the insulin $[M - 5H]^{5-}$ anion.

Interestingly, we thus find the double photodetachment energy threshold at ~ 2.8 times that for the single photodetachment, a figure that matches the empirical rule derived for double ionization of neutral molecules [42].

Two mechanisms may account for this double-electron ejection, even if the presence of an edge immediately suggests a direct process of single-photon double photodetachment, in analogy to direct double photoionization. However, a two-step mechanism may also occur, in which the product ion from single photodetachment $[M - 5H]^{4-\bullet}$ is stored long enough to reabsorb another photon and then lose the additional electron leading to $[M - 5H]^{3-\bullet\bullet}$. Indeed, longer irradiation times lead to the production of $[M - 5H]^{3-\bullet\bullet}$ below the 11.4 eV threshold. The ion abundance of this ion has been recorded as a function of the irradiation time at 8 and 15 eV photon energy, as shown in figures 3(a) and (b), respectively. A nonlinear increase with the irradiation duration in the ion abundance can be observed for both 8 and 15 eV (figure 3) and corresponds to indirect processes. Both ion abundances at 8 and 15 eV have been fitted with a second-order polynomial function: $a + bt + ct^2$, where t represents the irradiation time and a , b and c are the fit parameters. The linear parts from the polynomial function ($a + bt$) have been plotted as dotted lines in figures 3(a) and (b). It appears that for 8 eV photon energy (figure 3(a)), the linear part of the polynomial function is flat, with a zero slope (b parameter) and a nearly zero intensity (parameter a) accounting for the vanishing non-zero background observed below 11.4 eV in figure 2(b). This clearly indicates that observation of double photodetachment at 8 eV, and by extension below the 11.4 eV threshold, comes from the sequential two-photon mechanism with a pure quadratic dependence with irradiation duration. In contrast, at 15 eV, for low irradiation duration (i.e. below 100 ms), the data are adequately fitted by a linear function. In this range, the direct one-photon process is dominant. At larger irradiation time, the trend becomes nonlinear and the sequential two-photon mechanism is favored. The relative cross section obtained in figure 2 has been acquired at 90 ms irradiation time corresponding to the linear regime. Hence, for 90 ms irradiation time, the double photodetachment relative cross section of figure 2 may entirely be ascribed to a valence direct DPD.

In order to examine the crucial issue of sequential versus direct processes by another methodology, we have measured the photodetachment yields for the photodetachment

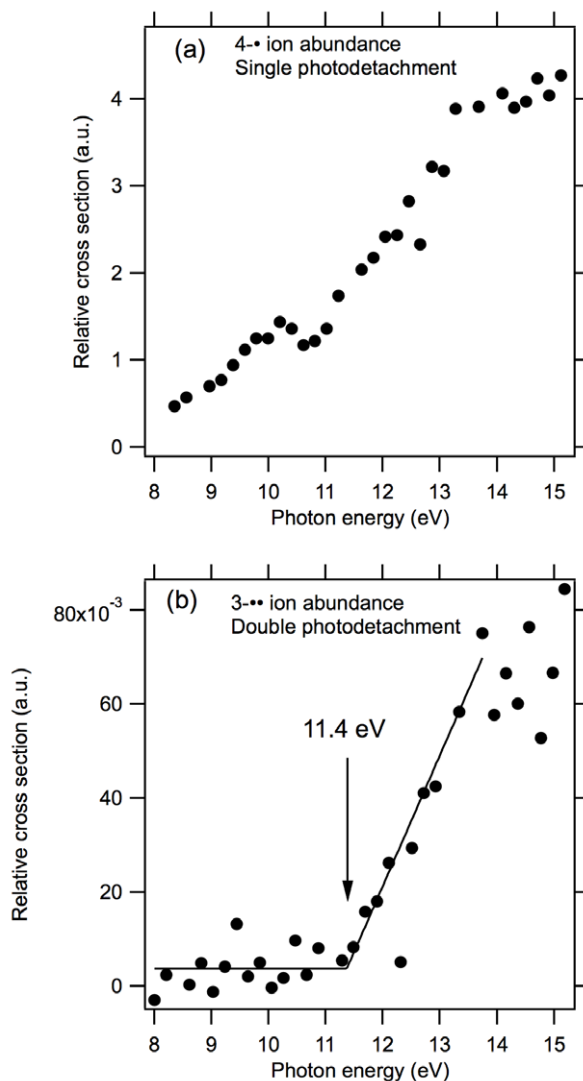
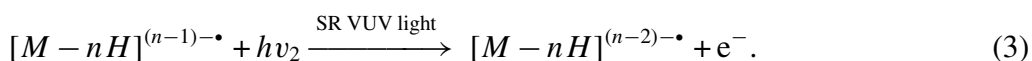
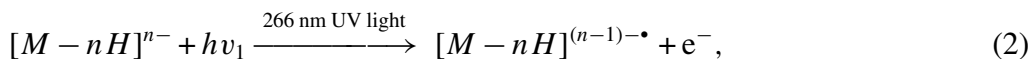


Figure 2. Partial relative cross section (see text) in the 8–15.2 eV range for 90 ms irradiation duration for (a) single photodetachment and (b) double photodetachment. The solid line is a Wannier-type linear fit to the data (see text).

$[M - nH]^{(n-1)-\bullet}$ oxidized products in a two-color scheme experiment [36, 37]:



The photodetachment yield measured as in equation (3) for the photogenerated $[M - nH]^{(n-1)-\bullet}$ radical (equation (2)) was compared with that of the corresponding closed-shell species $[M - (n-1)H]^{(n-1)-}$ in figure 4. It appears clearly in figure 4 that the oxidized products $[M - nH]^{(n-1)-\bullet}$ which are susceptible to re-absorbing a second photon, have qualitatively very similar absorption yields as their precursor ions. Figure 4 shows that photodetachment phenomenologically depends neither on the charge state nor on the oxidation state. The ion

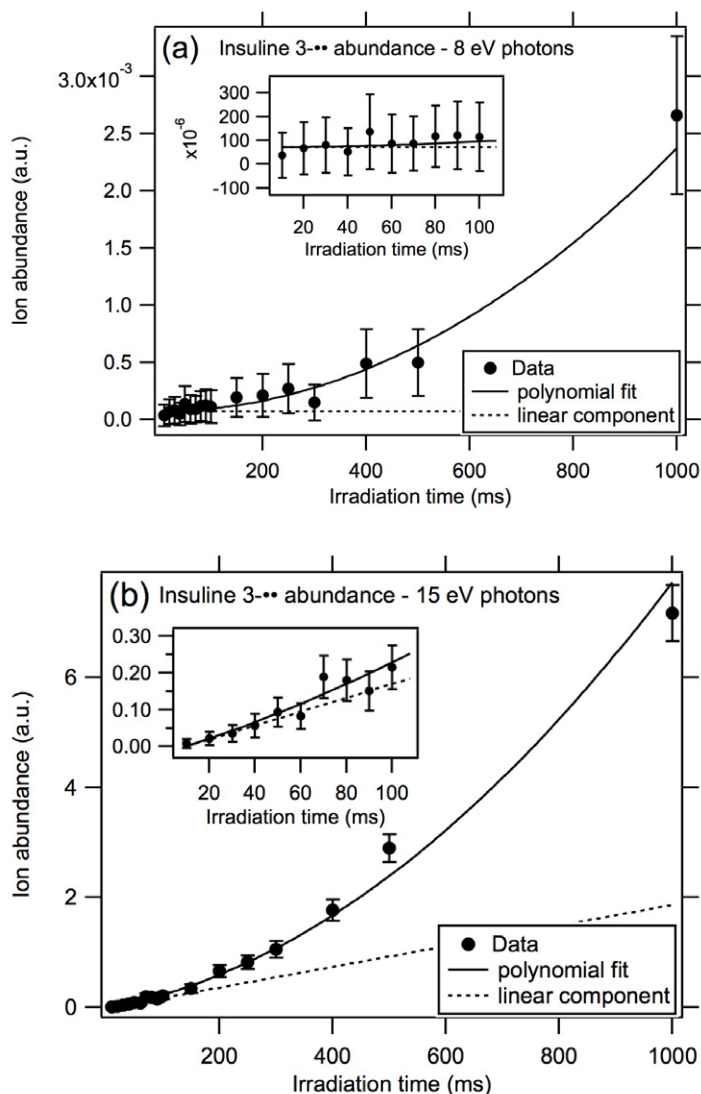


Figure 3. Ion abundances for the double photodetachment product ion $[M - 5H]^{3-\bullet\bullet}$ at (a) 8 and (b) 15 eV recorded as a function of the irradiation time in the 10–1000 ms range. The data were least square fitted by a second-order polynomial: $a + bt + ct^2$, where a , b and c are fitting coefficients and t stands for time in ms. The dotted lines labeled on the graph as a linear component represent the linear components of the fit expressed by $a' + b't$.

yield of the sequential two-photon process is described by the convolution of the yields for the two one-photon processes. Hence, if the double detachment product $[M - 5H]^{3-\bullet\bullet}$ was to be formed by the sequential two-photon mechanism, a non-negligible ion abundance should be detected in photon energy regions where the single photodetachment product $[M - 5H]^{4-\bullet}$ is formed in high yields, such as around 10 eV. This is not the case, since it is impossible that convolution of the photodetachment yields from figure 4 would generate a threshold behavior such as the one observed in figure 2.

The two methodologies related to figures 3 and 4 rule out the presence of a sequential process and the double photodetachment observed in figure 2, corresponding to a short

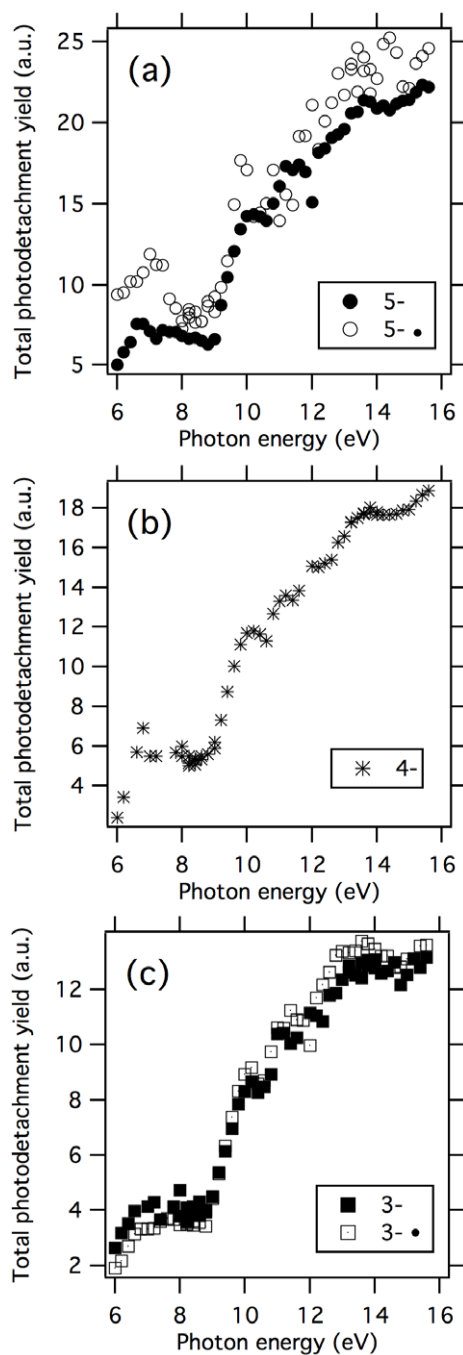


Figure 4. Total photodetachment yields as a function of the photon energy as calculated by $-\ln(\text{precursor}/(\text{precursor} + \text{products}))/\varphi$, where φ is the photon flux, ‘precursor’ is the intensity of the parent peak and ‘products’ represents the total intensity of the peaks corresponding to the oxidized species (i.e. protein that has lost electrons). Yields are compared for closed-shell precursors with 3-, 4- and 5-charge states and for open-shell precursors labelled 3 – • and 5 – •.

irradiation duration, is ascribed entirely to a single-photon absorption direct mechanism. This is the first report of direct double photodetachment. Also, to our knowledge, it is the first observation of direct multiple photodetachment occurring in the valence region in a protein polyanion. At 15 eV, and for short irradiation durations, double photodetachment amounts to $\approx 2\%$ of the detachment cross section, a figure that is quite similar, for the same excess energy above the DPD onset, to the one measure for double ionization of large organic molecules [14], and that should increase with the photon energy. Several processes might account for DPD as reported for the Cl^- anion, which is the most strongly bound atomic anion with a comparable electron affinity to those of peptides [11]. However, the intra-molecular knock-out process is certainly not the dominant mechanism. Indeed, it involves electron–electron collisions whose cross sections are expected to be low owing to the large distance between the negative charges spread over the protein. Following the previously described resonant mechanism for single photodetachment [35], we may postulate that double photodetachment could arise from one-photon double excitation of two electrons followed by relaxation with the emission of two electrons. Another possibility would be a one-photon single excitation of one electron that would autoionize into the double photodetachment continuum. However, the DPD threshold value appears to match the sum of the electron affinity of the carboxylate (~ 4 eV) [35] and the adiabatic ionization energy of aromatic amino acids (7.44 eV for tyrosine, 8.5 eV for phenylalanine) [43]. Thus, it may be suggested that DPD is observed when the ionization threshold is overcome (which releases a photoelectron) but with enough energy for a second electron to be detached. This tentative interpretation is consistent with the literature mechanism accepted for single photodetachment of protein poly-anions.

Another way of testing the DPD mechanism is through *ab initio* calculations. Since insulin is too large, a smaller model system, i.e. a 3-deprotonated tetrapeptide tri-anion $[\text{Gly-Glu-Gly-Tyr-3H}]^{3-}$, was chosen, for qualitative purposes. The structures of the tri-, di- and mono-anions were optimized at the RI-(U)MP2/cc-pVDZ level, using the Turbomole package [44]. The singlet tri-anion is stable, the HOMO being localized on the π molecular orbital of the tyrosine cycle. However, its vertical ionization energy is only 0.37 eV. Adiabatically, the doublet di-anion lies only 0.05 eV above the tri-anion ground state. These results are very similar to those obtained by Feuerbacher and Cederbaum on the $\text{B}(\text{C}_2\text{CO}_2)_3$ tri-anion [45]. The vertical ionization energy of the di-anion, leading to the singlet mono-anion, is predicted to be 1.92 eV (2.25 eV for the triplet state). Interestingly, the vertical double ionization thresholds producing the mono-anion directly from the tri-anion are 2.86 eV (triplet) and 4.50 eV (singlet). Thus, a single photon with these energies could be sufficient to produce an auto-ionizing state leading directly to the mono-anion. In the case of insulin, this threshold would be 11.4 eV. These calculations show at least that this double-electron photodetachment is energetically possible [40], and the difference in threshold values is at least partially due to the difference in excess charge density between the two systems, which is much lower for insulin.

A particularity of biomolecular polyanions (DNA, acidic proteins, heparins, etc) is that they have numerous electrons with low binding energies. This accounts for the possibility of sequential electron detachment with low-energy photons and makes them good candidates for direct multiple-electron detachment, as observed here. Polyanions are ubiquitous in the biosphere and are thus possible sources of low-energy electrons, a key issue in the field of radiation damage [46]. The energy correlation between the two emitted electrons and the exact electronic structure of the product ion will have to be studied in detail in the future. Indeed, a striking observation is the relative stability of the double photodetachment product ion on the

time scale of the experiment, as little fragmentation is observed on the mass spectra (figure 1) for highly excited species. Acidic biomolecules appear to be highly stable to following absorption of energetic electromagnetic radiation even after multiple photodetachment.

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