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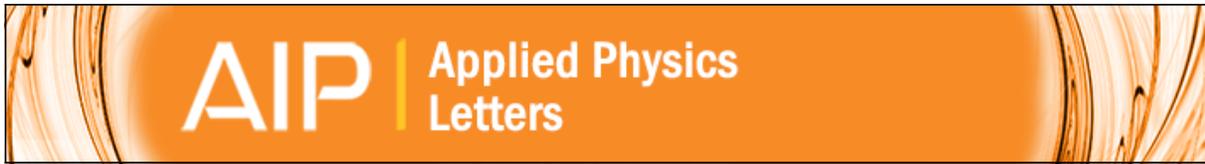
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Electron impact action spectroscopy of mass/charge selected macromolecular ions: Inner-shell excitation of ubiquitin protein

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We have performed inner-shell electron impact action spectroscopy of mass and charge selected macromolecular ions. For this purpose, we have coupled a focusing electron gun with a linear quadrupole ion trap mass spectrometer. This experiment represents a proof of principle that an energy-tunable electron beam can be used in combination with radio frequency traps as an activation method in tandem mass spectrometry (MS²) and allows performing action spectroscopy. Electron impact MS² spectra of multiply protonated ubiquitin protein ion have been recorded at incident electron energies around the carbon 1s excitation. Both MS² and single ionization energy dependence spectra are compared with literature data obtained using the soft X-ray activation conditions. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4941798>]

There has been a long standing effort to develop experimental techniques to investigate photon and electron interaction with large molecular species and complex systems under controllable, well-defined and single-collision conditions.^{1–4} In this respect, an important breakthrough has been made in recent years by successful coupling of synchrotron radiation sources with ion traps, to perform photon activation of mass over charge (*m/z*) selected ions confined in the gas phase.^{5–9} Indeed, by using electrospray ionization (ESI) technique¹⁰ to extract macromolecular ions from solution, tandem mass spectrometry (MS²)¹¹ and action spectroscopy^{3,12} of unprecedentedly large species could be performed. Recently, we have applied near-edge X-ray fine structure (NEXAFS) action spectroscopy to investigate interplay between the electronic and the three-dimensional structure of gas phase ubiquitin protein.¹³

However, electron impact activation MS² of large biopolymer ions trapped in a radio frequency (RF) ion trap, and corresponding electron impact action spectroscopy, is considerably more challenging. Indeed, in contrast to photons, electrons are very sensitive to the oscillating electric field. Depending on the incident electron energy, RF can strongly influence spatial and energy profiles of an electron beam and ultimately prevent the electrons entering the trapping region. Moreover, both primary and scattered electrons (from background gases and surrounding surfaces) can be extracted towards ion detectors (as composed of conversion dynodes and electron multipliers), inducing a significant noise in the recorded mass spectra or even damage the detectors. All these issues have certainly penalized the use of an energy-tunable focused electron beam as activation technique in MS² based on RF ion traps. It should be noted, however, that since the invention of electron capture dissociation (ECD),¹⁴ low-energy electron attachment to macromolecular ions has become a widely used activation method in MS² increasing

the potential of top-down protein sequencing.¹⁵ Using higher energy electrons, electron impact ionization of multiply protonated ions could be also achieved in Fourier transform ion cyclotron resonance (FT-ICR) ion trap instruments.¹⁶ Although electron activation techniques were originally performed using the FT-ICR trap, a great deal of research has been devoted in recent years to development of technical solutions allowing for efficient ECD in RF traps (see Refs. 17–20 and references therein). Still, all these reports are concerned with bringing low energy (close to 0 eV) electrons into an RF trap, in order to produce efficient fragmentation of macromolecular ions via electron attachment. Recently, Voinov and coworkers reported the implementation of a radio frequency-free analyzer-independent cell²¹ allowing ECD in triple quadrupole instruments. The method was also demonstrated in hybrid quadrupole time of flight instruments.²² Interestingly, low energy electron impact ionization could be achieved using this setup.

However, high-energy electron impact activation/spectroscopy of trapped ionic species has not been reported yet. This is surprising considering that the scientific community is appealing for a technique that would allow controllable investigation of electron interaction with macromolecular systems. Such measurements could open new spectroscopic investigations and shed new light on radiation damage research.¹ Also, profound understanding of electron interaction with complex exotic molecules could help development of new applications, such as Focused Electron Beam Induced Deposition (FEBID).²³ Finally, energy-tunable electron impact activation MS² allows fragmentation via selective inner-shell excitation of a macromolecule. This could open new possibilities for advanced top-down sequencing by loading incident energy into specific parts of the macromolecule or inducing preferential type of fragmentation via chosen resonant excitation.

In this letter, we present a system allowing energy resolved electron impact activation MS² of *m/z* selected protein ions confined in a RF linear quadrupole ion trap. The

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instrument is based on an energy-tunable focused electron beam providing incident electron energies around C K-shell excitation. We recorded MS^2 spectra at selected electron activation energies and performed action electron spectroscopy of trapped protein ions. Moreover, we report a comparative study of inner-shell protein ionization by electron impact and X-ray absorption.

The experiment was performed by coupling a commercial linear quadrupole ion trap mass spectrometer (Thermo Scientific LTQ XL), equipped with an ESI source, to a differentially pumped vacuum stage including a custom-made electron gun assembly. The electron gun and the corresponding assembly were developed at the Institute of Physics Belgrade (IPB), Serbia. The experiment was conducted at the DISCO beamline of the synchrotron SOLEIL, France, where the electron-LTQ XL assembly was constructed. Fig. 1 presents a schematic drawing of the experimental setup. Six-way CF100 cross was used as a vacuum chamber, which was mounted on a movable support, and connected to the backside of the LTQ XL mass spectrometer. The assembly holding the electron gun was mounted on a custom made CF100 flange, with electrical feed-through. The remaining flanges of the cross were used to fit a turbomolecular pump, a cold cathode ionization gauge, and a viewport. During the experiment, the pressure was 4×10^{-6} mbar in the cross and 1×10^{-5} mbar in the vacuum manifold of the LTQ XL. The coupling of the CF100 cross with the back plate of the mass spectrometer was achieved using a bellows, to allow precise alignment of the electron gun axis with respect to the ion trap axis. The LTQ XL mass spectrometer was also mounted on a dedicated custom-made movable frame allowing a fine tuning of the ion trap position, as previously used for alignment with the photon beam.²⁴ Therefore, optimal overlap between the electron beam and ion packet was achieved by both fine positioning of the mounting frames and steering of the electron beam using the XY deflectors. Prior to the experiment, a pre-alignment was performed by measuring incident electron current on an electrode installed temporarily behind the trap, downstream the electron beam (see Fig. 1).

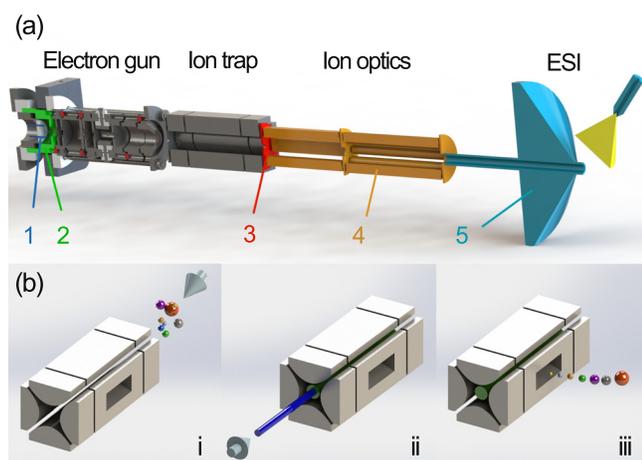


FIG. 1. Schematic representation of the experimental setup. (a) 1–tungsten filament, 2–Wehnelt electrode, 3–disc plate for current measurement, 4–quadrupole and octopole filters, 5–electrospray ion source. (b) i–ion injection and selection, ii–electron activation of selected ions, and iii–detection of fragments.

The electron gun was described in details previously.²⁵ Briefly, it consists of an extraction part and a focusing part (also including semi-cylindrically shaped XY deflectors to steer the beam). The electrons are emitted from a thoriated-tungsten cathode. The electron energy and all focusing voltages are controlled by a custom-made electronic board. The irradiation time was controlled by applying a variable DC pulse voltage on the Wehnelt electrode of the electron gun (see Fig. 1) that otherwise suppresses an electron emission from the filament. A dedicated electronic shutter circuit was designed in order to trigger and control the electron beam pulses by using the transistor-transistor logic (TTL) signal from the LTQ XL. The measurement procedure consisted of: ion production and injection into the trap, precursor isolation, electron irradiation, ion ejection, and detection, as previously used for photon irradiation.^{5,7,24} The shortest irradiation time can be set to a few tens of ms, but 500 ms was used in the present experiment. In order to reduce background contributions, the TTL signal from the LTQ XL was sent through a digital delay generator (DG645, Stanford Research Systems, Sunnyvale, CA, USA) that provides a short delay (usually adjusted to 200 ms) of the ion ejection, after the electron irradiation was stopped.

The main issue in this experimental concept is that a focused electron beam is introduced into a RF field, which can, in principle, strongly influence the beam properties. The LTQ XL quadrupole ion trap uses a combination of DC and RF voltages. The DC component is ± 100 V. The RF electric field has an amplitude of 400 V peak-to-peak and a frequency of 1 MHz.²⁶ Therefore, even for the shortest electron pulses of a few tens of ms, the electron beam appears as continuous for the RF performance (a full RF cycle is 1 μ s). Nevertheless, at the energy of about 300 eV, which is of interest for the present study (vicinity of C K-edge), an electron travels a half-length distance (34 mm) of the ion trap in about 5 ns. Therefore, we expect that a dominant portion of the incident electron current reaches the interaction volume almost undisturbed, while only small part is lost on the trap electrodes.

To investigate propagation and characteristics of the electron beam passing through the LTQ ion trap during 1 RF period, we performed electron tracing simulations using SIMION 8.2 program package²⁷ (Fig. 2). A continuous electron beam is simulated by a train of 1 ns pulses with 121 electrons arranged in a 0.5 mm square grid, which simulates a realistic electron current of 75 nA. Figs. 2(b) and 2(c) show simulated radial and kinetic energy distributions, respectively, of the electrons that can reach the center of the trap, for the starting energy of 300 eV and the initial beam radius of 0.5 mm. The simulations show that both the geometrical beam profile and the initial energy spread (limited to about 0.5 eV due to the emission from a hot cathode) are largely preserved in the interaction region, even though some disturbance due the RF field is inevitable.

Fig. 3(a) presents an electron activation MS^2 spectrum of multiply protonated ubiquitin protein ion (precursor charge state 7+) after electrospray ionization measured at 288 eV incident electron energy. Besides the peak corresponding to the precursor ion $[M+7H]^{7+}$ at m/z 1225, the dominant peak in the electron impact MS^2 lies at m/z 1071,

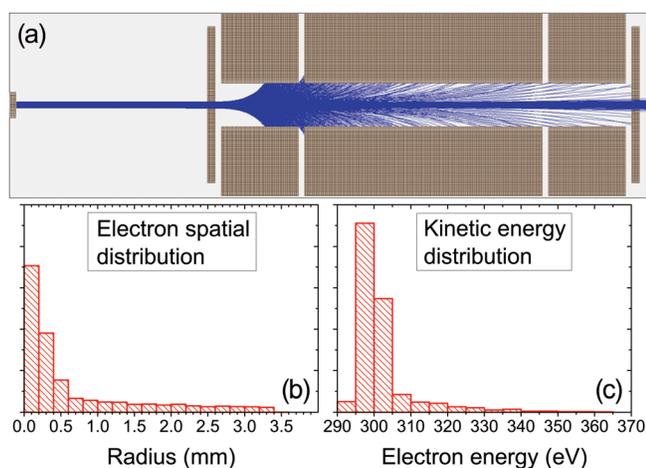


FIG. 2. Simulation of pulsed electron beam propagation in a linear quadrupole ion trap under influence of RF (1 MHz, 400 V) and DC (100 V) potentials. A total of 1.2×10^5 electrons, during a pulse width of $1 \mu\text{s}$, at the energy of 300 eV and with a beam diameter of 0.5 mm, was directed along the axis of the ion trap. (a) The simulation of the propagation of the electron beam; (b) the spatial distribution, and (c) the energy distribution of electrons recorded at the center of the ion trap.

which represents a radical singly ionized cation $[\text{M}+7\text{H}]^{8+}$. We ascribe the other closely positioned intensive peak at about m/z 1066 to a small neutral loss from the ionized $8+$ ion. Due to limited mass resolution for such high charge states, we cannot exactly define the mass of the neutral loss. We can tentatively assume that it could be due to amino acids side chain losses.¹² Finally, besides the single

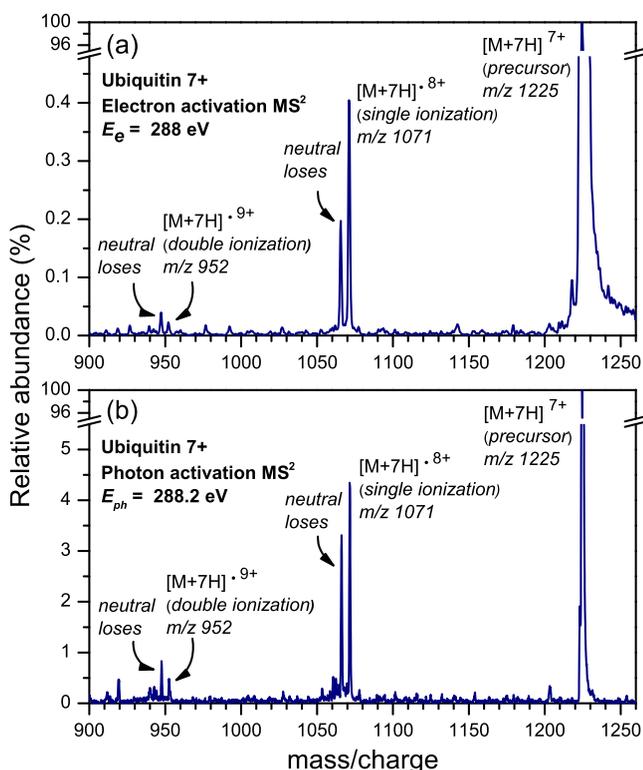


FIG. 3. Comparison of tandem mass spectra of Ubiquitin $7+$ precursor for energies near carbon K-edge activated with: (a) electrons (isolated m/z 1222.8–1225.8) and (b) photons (isolated m/z 1223.4–1226.4). The electron irradiation was performed during 500 ms (200 ms acquisition delay), with estimated 10^{13} electrons/second. The photon irradiation was performed during 600 ms (50 ms acq. delay), with estimated 10^{12} photons/second.

ionization (SI) process, which is clearly the dominant relaxation channel upon inner-shell electron impact excitation of ubiquitin, the peak corresponding to doubly ionized cation $[\text{M}+7\text{H}]^{9+}$ can also be traced down in the MS^2 at m/z 952. And the latter is accompanied by intensive neutral losses, as well. The abundances of other fragments are much lower and thus will not be discussed in the present study. It should be noted, however, that low-mass background was also detected (not shown here) and removed, most probably originated from electron ionization of neutral gases present in traces in the trap and the electron-induced noise.

For comparison, Fig. 3(b) presents X-ray activation MS^2 of the same $7+$ precursor and at practically the same photon energy of 288.2 eV. The results are extracted from recent X-ray inner-shell spectroscopy of gas-phase proteins by coupling the same ion trap to the PLEIADES soft X-ray beamline at the SOLEIL facility¹³ (note that the X-ray spectrum was measured with higher m/z resolution). The correspondence between the two spectra is striking. Indeed, the ionization of the protein is the result of the resonant Auger decay process, triggered by carbon 1s electron excitation to a frontier molecular orbital and a core hole formation. The ionization/fragmentation pattern, however, does not depend significantly on the triggering process itself.¹³ This finding is also important for the studies on radiation damage of proteins, particularly considering recent results suggesting that proteins were damaged by X-ray radiation at a faster rate than is DNA.²⁸

Nevertheless, it should be pointed out that the two discussed processes—electron and photon inner-shell excitation—are intrinsically different. In the case of X-ray activation, an incident photon is resonantly absorbed at the energy that corresponds to the transition involving a core electron. In the case of electron impact activation, the incident electron transfers part of its energy to the system triggering the electronic transition and is scattered out suffering the corresponding energy loss. Furthermore, in the present experiment, the incident electron energy is only slightly above the transition energy. Therefore, the electron excitation is performed under so-called near-threshold conditions.²⁹ Consequently, the acquisition of MS^2 as a function of the electron energy, in the same way as we measured action NEXAFS spectra of gas phase protein,^{7,13} will yield in the present case the action near-edge electron excitation function (NEEEF).

Fig. 4 presents NEEEF (circles) and NEXAFS (dashed line)¹³ action spectra of ubiquitin $7+$ precursor. In both cases, an area under the peak in MS^2 corresponding to singly ionized radical $[\text{M}+7\text{H}]^{8+}$ (see Fig. 3) has been normalized to the total ion current, and plotted as function of the activation electron or photon energy, respectively. In the case of the NEEEF spectrum, the focal properties of the electron gun are adjusted as a function of the electron energy to preserve a constant beam profile. These focusing voltages have been determined prior to MS^2 experiment by measuring electron current passing through the ion trap. Experimental details about the NEXAFS spectra are given in the previous publication.¹³ The spectra presented in Fig. 4 are normalized to the same area under the curve.¹³ The electron-induced SI yield is measured with lower energy resolution, which is due to

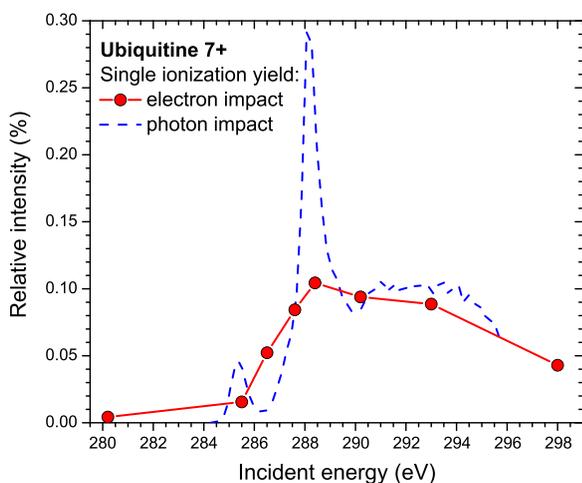


FIG. 4. Comparison of single ionization yield from Ubiquitin 7^+ precursor activated with electrons (red circles) and soft X-ray photons¹³ (blue dashed curve).

both using of an electron gun (without an electron monochromator) and additional beam energy broadening inside an RF trap (see Fig. 2).

The electron impact SI yield of ubiquitin protein (Fig. 4, circles) shows strong incident energy dependence. The cross section starts increasing at the energy that corresponds to $C\ 1s \rightarrow \pi^*_{\text{aromatic}}$ transition at about 284.5 eV and steeply rises reaching a maximum at about 288 eV, which corresponds to $1s \rightarrow \pi^*_{\text{amide}}$ transition. The SI yield slowly decreases with further increasing of the impact electron energy. There is a clear correspondence between the two sets of results obtained using X-ray or electron irradiation. Indeed, in both cases, the SI of the precursor proceeds from carbon core excited molecular transient state via Auger decay. Nevertheless, as already pointed out, the excitation processes itself is essentially different. Therefore, the electron energy dependence may be distinctly different, since in the electron impact case, a triggering process is due to near-threshold electron collision. Moreover, scattered electrons carry out some residual energy and the core excitation does not have to be resonant, so at a particular impact energy, it depends on the redistribution of excitation cross sections. It should be noted that previously, Cooper *et al.*³⁰ performed the inner shell electron energy-loss spectroscopy of a condensed protein, but recorded under scattering conditions where electric dipole transitions dominate (2.5 keV residual electron energy and 2° scattering angle). Such spectra, however, are to be compared with X-ray absorption data, as represented here by action NEXAFS spectrum (blue curve).

In conclusion, we have demonstrated energy-tunable focused electron beam activation of m/z selected trapped protein ions by coupling an electron gun to a linear quadrupole ion trap mass spectrometer. We have shown that both electron and X-ray activation produce very similar MS^2 patterns, which is defined by resonant Auger decay process regardless of triggering process. However, the energy dependences are not to be directly compared, since in the case of electron action spectroscopy, an electron impact near-threshold excitation takes place. Therefore, the present experiment suggests a possibility to perform a comparative

study of electron and photon induced excitation of macromolecular ions and to discuss intrinsic differences between the two processes, which will be undertaken in future publications.

The present results pave a way to developing methods for investigation of electron interaction with macromolecules, complex systems and nanoparticles, under well-defined conditions, and in a wide energy range. Moreover, we demonstrate a proof of principle for an activation method for MS^2 top-down macromolecular sequencing using high-energy electron impact activation of trapped ions. This may be a complementary low-cost method that allows investigating only specific fragmentation processes, depending on the activation energy.

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