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On the production of N_2^+ ions at the N 1s edge of the nitrogen molecule

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Abstract

The N_2^+ ion yield of the N_2 molecule has been measured at the N 1s \rightarrow Rydberg excitations. It displays Fano-type line shapes due to interference between direct outer-valence photoionization and participator decay of the core-excited Rydberg states. The N_2^+ ion yield is compared with the total intensity of the outer-valence photoelectron lines obtained recently with electron spectroscopy (Kivimäki *et al* 2012 *Phys. Rev. A* **86** 012516). The increasing difference between the two curves at the higher core-to-Rydberg excitations is most likely due to soft x-ray emission processes that are followed by autoionization. The results also suggest that resonant Auger decay from the core–valence doubly excited states contributes to the N_2^+ ion yield at the photon energies that are located on both sides of the N 1s ionization limit.

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

1. Introduction

Photoabsorption spectra of atoms and molecules show discrete resonances below core ionization potentials (IP). Those resonances represent the creation of highly excited neutral states, where an inner-shell (or core) electron has been transferred to an unoccupied (or virtual) valence or Rydberg orbital. The resulting core-excited states decay very fast—typically in the fs range—by emitting x-ray photons or electrons or, in some cases, they may dissociate before the decay of the core hole (ultrafast dissociation [1]). Electron emission is by far the predominant decay channel in molecules composed of light elements such as carbon, nitrogen and oxygen. In this so-called resonant Auger decay, one valence electron fills the core hole, while another valence electron is emitted. More specifically, in participator (resonant Auger) transitions, the electron that was promoted to the unoccupied

orbital takes an active part in decay, which leads to the same valence one-hole (1h) states that are reached in direct valence photoionization. In spectator (resonant Auger) transitions, the orbital accessed in the excitation process remains occupied also after the decay, whereas two holes are created in valence orbitals; such final states can be denoted as 2h–1e states. Thus the final states of resonant Auger transitions are, in general, singly charged. While 1h states are often bound in small molecules, 2h–1e final states typically (but not always) dissociate because of the double-hole valence configuration. The sum of the charge states of the fragments must equal +1; hence singly charged cations and neutral fragments are expected to be the most common dissociation products after resonant Auger decay, see e.g. [2, 3]. More highly charged ions can be created when core-excited states decay by emitting two or more electrons simultaneously (double and triple Auger decay [4]) or when they decay to so highly excited ionic

states that second-step Auger decay is energetically allowed (Auger cascades). Autoionization in an excited fragment after molecular dissociation can also occur and increase the charge state of the fragment, see e.g. [5].

The inner-shell absorption spectrum of the N_2 molecule [6, 7] displays the well-known $N\ 1s \rightarrow \pi^*$ resonance around 401 eV excitation energy. It is followed by the $N\ 1s \rightarrow$ Rydberg excitations that converge to the $N\ 1s$ ionization limits at 409.82 and 409.93 eV [8]. Furthermore, the core excitation spectrum of N_2 is exceptional because it contains core–valence double excitations even below the $N\ 1s$ IP [9] where they overlap with ‘high’ core-to-Rydberg excitations (‘high’ means here that the principal quantum number n of the Rydberg electron is ≥ 4). In core–valence double excitations, a core electron and a valence electron are simultaneously promoted to unoccupied orbitals. N_2 is one of the most studied molecules with resonant Auger spectroscopy, but these studies have very much concentrated on the $N\ 1s \rightarrow \pi^*$ resonance, e.g. [10–14]. At that excitation, participator decay strongly populates the $X\ 3\sigma_g^{-1}$ and $A\ 1\pi_u^{-1}$ states of the N_2^+ ion, but hardly at all the $B\ 2\sigma_u^{-1}$ state [15]. These three states are stable; hence the parent ion, N_2^+ , is abundantly observed at the $N\ 1s \rightarrow \pi^*$ resonance [10, 16, 17]. Spectator decay is, however, even more important than participator decay, making the N^+ ion by far the dominant ionic fragment [10, 16]. It is generally considered that participator decay is very weak or even negligible from core-to-Rydberg excited states. Indeed, the ion-mass spectroscopy studies performed in the 1980s and 1990s [16, 17] did not reveal any enhancement in the parent ion yield in the energy range of the $N\ 1s \rightarrow$ Rydberg resonances. The photoelectron spectroscopy measurements of Kugeler *et al* [18], however, showed that the photoionization cross sections of the outer-valence photoelectron bands deviate from their long-range behaviour at core-to-Rydberg resonances, implying that participator decay may play a role in the decay of such core-excited states. We recently undertook a systematic study of the valence photoelectron spectrum in the $N\ 1s$ threshold region and observed that the intensities of the X and A states display clear Fano line shapes as a function of photon energy [19]. As the X and A states of N_2^+ are bound, this observation clearly disagreed with the previous mass spectroscopy results [16, 17]. In this work, we have complemented the photoionization study [19] by measuring the N_2^+ partial ion yield of the N_2 molecule across the $N\ 1s$ edge. We find that the N_2^+ ion yield is greatly affected by the $N\ 1s \rightarrow$ Rydberg excitations. We also consider the possibility that parent ions are produced in decay pathways involving soft x-ray emission from the core-to-Rydberg excited states and resonant Auger decay from the core–valence doubly excited states.

2. Experiment

The experiments were performed at the Gas Phase Photoemission beamline at the Elettra synchrotron radiation laboratory in Trieste, Italy. The beamline has been described before [20]; therefore only the main features are given here. Synchrotron radiation from an undulator with the magnet period of 12.5 cm is monochromatized by a spherical grating

monochromator that is equipped with a plane pre-mirror. High photon energy resolution ($h\nu/\Delta h\nu \geq 10^4$) can be achieved in most of the photon energy range from 14 to 900 eV by selecting one of the five interchangeable gratings.

An ion time-of-flight (TOF) mass spectrometer was mounted in the dipole plane at the so-called magic angle (54.7°) with respect to the electric vector of the incident light. That angle was chosen because it was advantageous for electron spectroscopy measurements that were carried out during the same experimental session; see below. The ion TOF spectrometer itself has the acceptance angle of 4π for ions whose velocities are below a certain limit. The limit is determined by the detector size of the ion TOF spectrometer, the length of the instrument (the drift tube is 320 mm long) and the applied electric fields in the interaction region, and corresponded to the kinetic energy of about 4 eV for N^+ ions under the used experimental conditions. The ion TOF spectrometer offers the time-resolving power $T/\Delta T$ of about 175 [21]. The sample gas was introduced into the interaction region through a hypodermic needle. The pressure in the chamber was 1.3×10^{-6} mbar during the measurements, but it is estimated to be about ten times higher in the interaction region where the monochromatized photon beam crossed the effusive gas jet. Ions created after interaction with the soft x-rays were extracted by applying pulsed voltages in the repeller and extractor meshes at the frequency of 4000 Hz. The electric field, when switched on, had the strength of about 400 V cm^{-1} in the interaction region. The rising edge of the pulsed voltage provided the start signal, while the arrival of ions in a microchannel plate detector gave the stop signals. The start and stop signals were fed into a time-to-digital converter system (ATMD-GPX from ACAM⁶) in order to record the arrival times. The photon energy was scanned with ~ 35 meV energy steps across the Rydberg resonance region and a TOF spectrum was collected for 5 min at each point. The photon energy resolution was about 60 meV in these measurements. The photon energy scale has been calibrated to the literature values of the core-to-Rydberg excitations [7].

Additionally, the resonant Auger spectrum of the N_2 molecule was measured at the $N\ 1s \rightarrow 3s\sigma$ Rydberg excitation using a commercial hemispherical electron analyser (VG i220). The analyser was mounted at the magic angle in the dipole plane and opposite to the ion TOF spectrometer. This angle ensures that the observed intensity distributions of the electrons are equal to the angle-integrated ones [22]. In the measurement of the resonant Auger spectrum, the kinetic energy resolution of the analyser was about 0.6 eV and the photon energy resolution was ~ 0.12 eV.

3. Results and discussion

Figure 1(a) shows the ion TOF spectrum measured at the most intense Rydberg excitation, the $N\ 1s \rightarrow 3p\pi$, which is located at the energy of 407.16 eV [7]. The spectrum shows three peaks that can be attributed to the parent ion (N_2^+), to the overlapping contributions of N^+ and N_2^{2+} as well as to N^{2+} . Higher charge states were not seen, which is in agreement with the fragmentation study of Saito *et al* performed at

⁶ ACAM Messelectronic GmbH. www.acam.de.

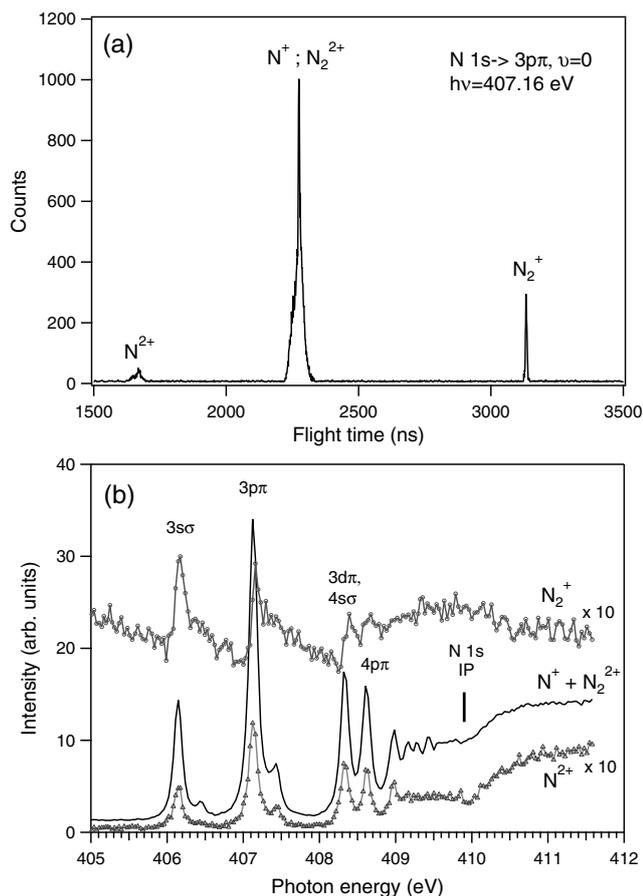


Figure 1. (a) Background-subtracted ion TOF spectrum of N_2 measured at the photon energy of 407.16 eV. Counts refer to ions detected in 1 ns wide windows. (b) Relative partial ion yields of N_2^+ , ($N_2^+ + N^+$) and N^{2+} at the N 1s edge of N_2 . The most intense N 1s \rightarrow Rydberg excitations have been assigned according to [7]. The partial ion yields of N_2^+ and N^{2+} have been multiplied by a factor of 10. Note that some fast N^{2+} and N^+ ions escaped detection; see text for details.

the N 1s $\rightarrow \pi^*$ resonance [23]. The authors of that study also reported coincidences between different ion pairs up to $N^{2+}-N^{2+}$. We determined the partial ion yields from the ion TOF spectra measured at the N 1s edge by integrating the counts over the peaks and by normalizing these counts to the photon flux that was measured simultaneously. The results are shown in figure 1(b).

Suzuki and Saito observed [16] that the mean kinetic energy of N^{2+} ions is about 10 eV at the N 1s edge, but some N^{2+} ions have kinetic energies even above 20 eV. According to ion trajectory simulations performed with the Igor program,⁷ 10 and 69% of the N^{2+} ions are lost in the present experiment if their kinetic energies are 10 and 20 eV, respectively (an isotropic angular distribution for the ions' initial velocities was assumed). This is because the momentum of the ions perpendicular to the instrument axis is so high that their trajectories do not bend sufficiently in order to enter the drift tube of the ion TOF spectrometer or to hit the detector. N^+ ions are slower: their most likely kinetic energy is 4–6 eV at different excitation energies at the N 1s edge of N_2 [16]. Our simulations indicate that 13% of N^+ ions with 5 eV kinetic energy escaped detection in the present experiment.

⁷ <http://wavemetrics.com>. A macro developed by E Kukku was used.

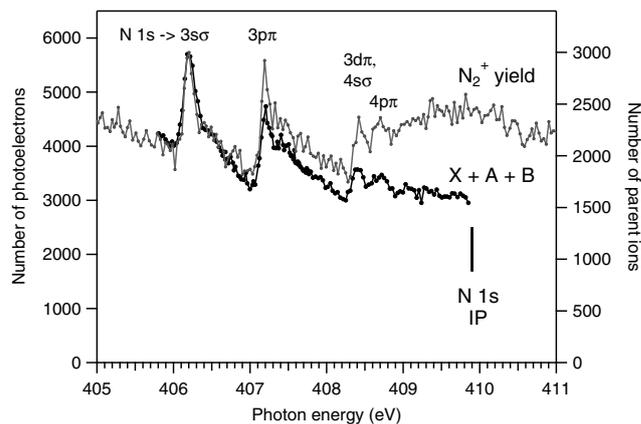


Figure 2. The sum intensity of the X, A and B photoelectron peaks (black dots, from [19]) is compared with the N_2^+ ion yield in the N 1s threshold region.

Therefore, our yield curve for the sum of N^+ and N_2^{2+} is biased towards N_2^{2+} , which only has thermal kinetic energy and cannot escape the extraction field. N^+ ions still account for the major part of the ions detected in our experiment because the branching ratio of N^+ is of the order of 75% at the core-to-Rydberg resonances, while that of N_2^{2+} is 2–5% [16]. All parent ions, N_2^+ , are also pulled inside the ion TOF spectrometer and their detection is consequently favoured in our experiment. Under these circumstances it is not appropriate to give any branching ratios among the different ions, and in the following we concentrate on the parent ion yield.

N_2^+ ions are observed at all energies. Direct valence ionization is expected to give a slowly decreasing background level, but we see in figure 1(b) that the N 1s \rightarrow 3s σ and 3p π Rydberg excitations cause variations in the parent ion yield that are about half of the base level. The peak shapes in the parent ion yield are asymmetric, in contrast to those seen in the sum of N^+ and N_2^{2+} yields, and their maxima are slightly shifted to higher photon energies. These properties are characteristic of Fano resonances, which arise when direct and resonant photoionization channels interfere. The interference effects were recently studied by measuring the outer-valence photoelectron spectra of N_2 in the excitation energy range of the N 1s \rightarrow Rydberg resonances and by performing numerical simulations [19]. Figure 2 compares the parent ion yield with the outer-valence photoelectron intensity, which was calculated as the sum intensity of the X, A and B photoelectron lines from the results of [19]. The parent ion yield measured in this work is consistent with the observations done with electron spectroscopy [19]. The earlier mass spectroscopic studies [16, 17] reported flat intensity behaviour for the N_2^+ ions in the core-to-Rydberg region. It is not clear why the intensity variations in the N_2^+ ion yield did not show up in the measurements of [17] even though the photon energy resolution was sufficient for their observation.

The X, A and B states of N_2^+ are bound, so their population in photoionization and participator decay affects the parent ion yield. However, some 2h–1e final states populated in spectator transitions are expected to be stable or meta-stable, contributing also to the parent ion yield. This is because a vibrational structure has been observed for many doubly ionized states [24] and 2h–1e states have, in the first

approximation, parallel potential energy curves to those of the analogous 2h states. Therefore, in reality, the two curves in figure 2 should not be scaled at the same heights, as has been done at the N 1s \rightarrow 3s σ resonance. We can anyway compare their relative intensities. The sum of parent ions originating from photoionization to the X, A and B states decreases at the higher Rydberg excitations (3d π /4s σ , 4p π ,...) as compared to the N 1s \rightarrow 3s σ excitation and the deviation from the parent ion yield increases. The maxima of the 3d π /4s σ and 4p π resonances also slightly differ in energy in the two curves, but this is an instrumental artefact caused by the use of different parameters when scanning the monochromator. There are at least two possible reasons for the increasing deviation in the intensities. Spectator decay at higher core-to-Rydberg resonances could give proportionally more parent ions than at the 3s σ and 3p π Rydberg resonances. This would be at first sight surprising because the 2h–1e final states populated in spectator decay have higher binding energies (and are more likely to be above given dissociation limits), when the electron is promoted to a higher Rydberg orbital in core excitation. Such a trend could nevertheless appear if a 2h–1e final state possesses some dissociative character when the spectator electron is located in the 3s σ Rydberg orbital and to a lesser extent also in the 3p π orbital.

Another process that can affect the parent ion production occurs when soft x-ray emission from the core-excited states is followed by autoionization. The whole sequence of processes would be $N_2 + h\nu \rightarrow N_2(1s^{-1}Ryd^1) \rightarrow N_2(val_1^{-1}Ryd^1) + h\nu' \rightarrow N_2^+(val_2^{-1}) + e^-$, where val₁ and val₂ are two valence orbitals. This decay pathway was recently observed in the CO₂ molecule using x-ray emission–photoion coincidence spectroscopy [25]. Glans *et al* [26] have reported the soft x-ray emission spectra of N₂ at the N 1s \rightarrow π^* resonance as well as at the N 1s \rightarrow 3s σ and 3p π Rydberg excitations. At the N 1s \rightarrow 3s σ excitation, soft x-ray emission only reaches the 3 σ_g^{-1} 3s σ^1 state, which is located below the first ionization potential of 15.581 eV. At the N 1s \rightarrow 3p π excitation, a small part of x-ray fluorescence intensity goes to the 2 σ_u^{-1} 3p π_u^1 state, which, as judged by the transition energy, should be located above the IP and could thus be followed by autoionization to the ground state of N₂⁺. The soft x-ray emission energies are expected to remain practically constant at higher core-to-Rydberg excitations because the N 1s \rightarrow 3p π soft x-ray emission spectrum is shifted from the non-resonant spectrum, resulting from the (N 1s)⁻¹ states, by only 0.05 eV [26]. This means that the initial and final states of soft x-ray emission should increase by the same amount, when the higher core-to-Rydberg resonances are excited. Consequently, the relative portion of such 1h–1e final states of soft x-ray emission that are located above the first IP of N₂ should grow at the higher core-to-Rydberg resonances; that portion can autoionize to the X state of N₂⁺. This trend of increasing autoionization probability after soft x-ray emission would agree with the increase of the parent ion production at the higher core-to-Rydberg resonances.

Is the soft x-ray emission channel strong enough to cause visible changes in the parent ion yield? This can be estimated by comparing the probabilities of participator decay and soft x-ray emission at the N 1s \rightarrow Rydberg resonances. The K fluorescence yield of N atoms has been calculated

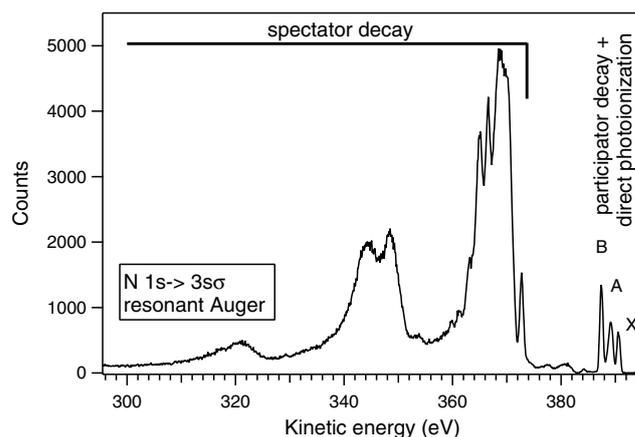


Figure 3. Resonant Auger spectrum of N₂ measured at the N 1s \rightarrow 3s σ excitation. Spectator decay is responsible for the main spectral features, while participator decay contributes to the intensities of the outer-valence photoelectron lines (X, A and B states).

to be about 0.5% [27]. The remaining decay probability (\sim 99.5%) should then be due to resonant Auger processes. The relative portion of the participator decay can be estimated from the resonant Auger spectra, but those numbers were not given in the published studies [5, 28]. We therefore show in figure 3 the resonant Auger spectrum measured at the N 1s \rightarrow 3s σ excitation. It is in good agreement with the spectrum of Eberhardt *et al* [28]. The spectral features below the kinetic energy of 374 eV are mostly caused by spectator transitions (or, more generally, by non-participator processes), but their assignment is beyond the scope of the present study. Participator decay and interference between direct and resonant photoionization channels modify the intensities of the outer-valence photoelectron lines [19]. The intensities to the X, A and B states of N₂⁺ were found to resonate at the N 1s \rightarrow 3s σ excitation. For a rough estimate, we assume that 30% of their intensity is due to the resonance (and the rest is due to direct photoionization). Integrating over the regions of interest in the spectrum of figure 3, we then obtain that participator decay accounts for \sim 1.0% of the resonant Auger intensity in the displayed kinetic energy window. This value is rather the upper limit, as the resonant Auger spectrum extends to even lower kinetic energies with gradually decreasing intensity. The portion of participator decay should be slightly lower at the other core-to-Rydberg resonances, where only the X and A states resonate and they do so more weakly [19] (see also figure 2). We thus arrive at the conclusion that participator decay and soft x-ray emission followed by autoionization are expected to have quite similar probabilities of producing N₂⁺ ions in the region of higher Rydberg resonances. We in fact suggest that the combination of soft x-ray emission and autoionization is responsible for the observed enhancement in the parent ion yield around the N 1s \rightarrow 3d π /4s σ and 4p π excitations. Previously, the intensity enhancement of the B–X visible fluorescence emission in the N₂⁺ ion observed around the σ^* shape resonance, which is above the N 1s IP, has been explained by soft x-ray emission from the 1 σ_g^{-1} state to the B 2 σ_u^{-1} state [18].

The wide bump in the parent ion yield at photon energies of about 408.5–410.5 eV (figures 1 and 2) is probably due to

core–valence double excitations [9, 29]. The existence of such states was concluded from the resonant Auger spectra: a decay feature was observed at the kinetic energy of ~ 384 eV that could not originate from singly core-excited or core-ionized states. The feature appeared to remain at a fixed position when the photon energy was changed. It was originally attributed to Auger decay in N atoms following ultrafast dissociation [9], but was later reassigned to the transitions to the $C^2\Sigma_u^+$, $D^2\Pi_g$ or $(2)^2\Pi_g$ states of N_2^+ [30]. The C and D states have a leading character of $2h-1e$ states [31, 32]; thus decay to them from core–valence doubly excited states involves one participator and one spectator electron. The lowest vibrational levels of the $C^2\Sigma_u^+$ and $(2)^2\Pi_g$ progressions [31] are located below the dissociation limit of 24.2884 eV for $N_2 \rightarrow N+N^+$ [33]. The measurements of Naves de Brito *et al* [30] clearly show that the spectral region just below this binding energy is resonantly enhanced at the photon energies of 409.2, 409.4 and 409.9 eV. That intensity is transferred into the N_2^+ partial ion yield. In particular, the $C^2\Sigma_u^+$, $D^2\Pi_g$ and $(2)^2\Pi_g$ states of N_2^+ can decay to the $X^2\Sigma_g^+$, $A^2\Pi_u$ and $A^2\Pi_u$ states, respectively, by emitting ultraviolet light [34, 35]. In principle, there should be interference between direct and resonant photoionization channels to the $C^2\Sigma_u^+$, $D^2\Pi_g$ and $(2)^2\Pi_g$ states of N_2^+ ; the resonant channels in question are due to core–valence doubly excited states. The interference effects are expected to be subtle in this case, as direct photoionization is much weaker than resonant photoionization [30], but they might be observable with photoelectron spectroscopy. A study of these interference effects with parent ion yield measurements is further complicated by the single $N\ 1s \rightarrow$ Rydberg excitations that are located in the same photon energy range. Core–valence doubly excited states may decay to some other $2h-1e$ states whose binding energy is above the $N_2 \rightarrow N+N^+$ dissociation limit, but which do not dissociate (at least not immediately). They could also decay to $1h$ states if both the electrons promoted to the virtual orbitals take part in resonant Auger decay (the process may be called double participator decay). That decay channel would be visible in the $(X+A+B)$ photoelectron intensity, but we do not see any conclusive evidence for it in the studied photon energy range in figure 2.

4. Conclusions

The N_2^+ partial ion yield of the N_2 molecule has been measured at the $N\ 1s$ edge with higher sensitivity and resolution than in the earlier studies. It displays clear Fano line shapes around the $N\ 1s \rightarrow 3s\sigma$ and $3p\pi$ Rydberg excitations, in agreement with the recently determined relative partial photoionization cross sections of the outer-valence photoelectron lines [19]. The Fano line shapes are visible in the parent ion yield because direct photoionization and participator decay of the core-to-Rydberg excited states populate the same bound $1h$ states—most importantly the X, A and B states—of N_2^+ with similar strengths. We also argue that the decay of core-excited states by soft x-ray emission, followed by autoionization, can yield parent ions at the $N\ 1s$ excitations to higher Rydberg orbitals. An enhancement in the parent ion yield that is observed on both sides of the $N\ 1s$ IP is attributed to the decay of core–valence doubly excited states.

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