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Multiple Auger decays of core-excited states in N₂

Takeshi Odagiri^{a)*}, Takuro Taniguchi^{a)}, Tatsuo Kaneyasu^{b)}, Hirokazu Tanaka^{c)}, Jun-ichi Adachi^{c)}, Pascal Lablanquie^{d)} and Yasumasa Hikosaka^{e)}

^{a)} Department of Materials and Life Sciences, Sophia University, Tokyo 102-8554, Japan

^{b)} SAGA Light Source, Tosu 841-0005, Japan

^{c)} Photon Factory, Institute of Materials Structure Science, Tsukuba 305-0801, Japan

^{d)} Sorbonne Université, UPMC Univ Paris 06, CNRS, LCP-MR (UMR 7614), 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

^{e)} Institute of Liberal Arts and Sciences, University of Toyama, Toyama 930-0194, Japan

* odagiri.t@sophia.ac.jp

Abstract

Multi-electron coincidence measurements have been performed at the photon energies for the core-to-valence ($1s \rightarrow \pi^*$) and core-to-Rydberg ($1s \rightarrow 3s\sigma$ and $3p\pi$) resonant excitations in N₂, in order to investigate the dynamics of multiple Auger-electron emissions from these core-excited states in detail. Peaks due to slow electrons from superexcited atomic fragments are observed in the decay processes by emission of 2 or 3 Auger electrons, indicating stepwise (cascade) multiple Auger decays that involve faster dissociations than electronic relaxations. Energy partitions between the emitted electrons enable us to reveal the detailed decay mechanisms for these processes. Branching ratios among the decays by emission of 1, 2 or 3 Auger electrons and those between the simultaneous (direct) and stepwise (cascade) processes have been determined for each of the core excited states. Branching ratios of decay channels resulting in molecular or fragment ions have also been substantiated.

1. Introduction

In photoabsorption of an atom or molecule just below its K shell ionization threshold, resonant excitations of a core-electron into an unoccupied valence or Rydberg orbital take place. The core excited states relax predominantly by Auger electron emissions when the atom or molecule is composed of low- Z elements. The electron promoted in the initial photoexcitation can either participate or behave like a spectator in the Auger transitions, leading to increased varieties of decay routes as compared with the Auger processes of the core-ionized states formed above the K shell ionization threshold¹.

The Auger transition from such core-excited states often result in the emission of several electrons. Such processes are known as multiple Auger decays. In multiple Auger processes, more than two electrons may be emitted simultaneously (direct process) or sequentially (cascade process). Dynamics of the multiple Auger decays is more complicated and interesting for molecules than atoms since it additionally contains interplay between electronic and nuclear motions as demonstrated in CO by Kaneyasu *et al.*² However, the multiple Auger decays of molecular core-excited states remain little studied because efficient coincidence technique is required for a detailed understanding of the mechanisms.

In the present study we focused on the $1s \rightarrow \pi^*$, $1s \rightarrow 3s\sigma$ and $1s \rightarrow 3p\pi$ core-excited states in N_2 . The conventional Auger electron spectra of N_2 following these resonant excitations have been reported previously³⁻⁵. Spectra of slow electrons emitted as a consequence of the core-to-Rydberg resonant excitations in N_2 were measured with high energy resolution by Shigemasa *et al.*⁶ They observed peaks associated with autoionization of superexcited states in atomic nitrogen converging to the $N^+(2s^2 2p^2, ^1D^e)$ ionic state. From the analysis of the Doppler peak profiles, they also estimated the translational energy of the superexcited $N^*(4d, ^2F^e)$ fragment as ~ 5 and ~ 4 eV for the $3s\sigma$ and $3p\pi$ resonances, respectively. Ratios of all the produced ions and their kinetic energies from these core-excited states were measured by Suzuki and Saito⁷ by using a time-of-flight technique. They revealed that the ion branching ratio at the π^* resonance is considerably different from that above the ionization threshold. Iwayama and Harries⁸ recently performed Auger electron – ion coincidence measurements and obtained the spectra of Auger electrons tagged with the production of N_2^+ and N^+/N_2^{2+} from the π^* resonance.

In the present study, we have used a magnetic bottle electron spectrometer which has great efficiency for multi-electron coincidences. Detecting all emitted electrons in the single, double and triple Auger transitions enables us to obtain a deeper understanding of the whole relaxation mechanisms in the resonant excitations. Through careful analysis of the coincidence data, ratio of decay channels for the core-excited states has also been obtained.

2. Experiment

The experiments were carried out by using soft x-rays from a grazing incidence monochromator at the undulator beamline BL-16A⁹ of the Photon Factory, KEK. The storage ring was operated in the hybrid-fill mode¹⁰ with a top-up injection in which half of the storage ring was filled by a train of low current bunches and an isolated high-current bunch was located at the center of the opposite half. The high-current bunch provides light pulses of 1.6-MHz repetition rate. To obtain a repetition rate suitable for the present electron time-of-flight measurement described below and to cut-off the light pulses due to the low current bunch train, a mechanical pulse selector¹¹ whose rotation synchronizes with the RF signal of the storage ring was used. The pulse selector consists of a rotating disk having 360 slits of 50- μm width along its circumference and the resultant repetition rate of the light pulses is 146 kHz^{11, 12}.

The multi-electron coincidences were obtained by using a magnetic-bottle electron spectrometer. The details of the spectrometer and data acquisition scheme were described elsewhere¹³. In brief, the electrons emitted after photoabsorption were collected into a 2.5-m long time-of-flight tube by an inhomogeneous magnetic field applied to the ionization region. The collection efficiency of the electrons was nearly 100% for kinetic energies less than 400 eV. The overall detection efficiency of the electron was estimated to be approximately $0.5^{+0.1}_{-0.05}$ in the present measurements which was nearly equal to the open area ratio of the microchannel plate. The resolution for kinetic energy of electrons $E/\Delta E$ was approximately 50. The target N_2 molecules were supplied through a copper nozzle of 500 μm inner diameter. The coincidence measurements were done at photon energies of 401.08 eV ($\text{N } 1s \rightarrow \pi^*$), 406.15 eV ($\text{N } 1s \rightarrow 3s\sigma$) and 407.13 eV ($\text{N } 1s \rightarrow 3p\pi$). The locations of these core-excitations in the absorption spectrum are shown in figure 1. The photon energy bandwidths were set to less than 80 meV.

3. Results and discussion

The electronic configuration of the ground electronic state in N_2 is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2(1\pi_g)^0 X^1\Sigma_g^+$. The valence orbitals are classified into two: the inner valence $2\sigma_g$ orbital (iv') and the outer valence $2\sigma_u$, $1\pi_u$ and $3\sigma_g$ orbitals (ov'). The lowest unoccupied orbital is the $1\pi_g$ orbital which is referred to as π^* .

3.1 Resonant Double Auger decay

In a resonant double Auger (RDA) process two electrons are emitted simultaneously (direct

processes) or sequentially (cascade processes)^{2, 14}. In the former process the two outgoing electrons share the excess energy in the double ionization, i.e. $h\nu - BE(N_2^{2+}) = KE_1 + KE_2$, where $BE(N_2^{2+})$ is the binding energy of doubly charged ions with respect to the ground state of neutral molecule and KE_1 and KE_2 are the kinetic energies of the fast and slow electrons, respectively. A U-shaped energy distribution due to the relatively low probability of equal energy sharing ($KE_1 \sim KE_2$) is expected in the direct RDA process as was observed in the direct DA processes from the core-ionized state^{12, 15}. On the other hand, in the cascade RDA decay electrons have the kinetic energies corresponding to the energy differences between the initial and final states in each Auger step. When a prompt dissociation of the intermediate molecular ion takes place, the second electron emission can occur from atomic fragment. These different processes can be distinguished by examining the energy spectra of the two emitted electrons.

Figures 2(a) - 2(c) show the energy correlation maps for the two-electron coincidence events. The vertical axes are kinetic energy of slow electron (KE_2). The horizontal axes represent the photon energy minus kinetic energy of fast electron, $h\nu - KE_1$, which corresponds to the binding energy of the intermediate N_2^+ state in the cascade RDA processes. The direct processes are expected to appear on the lines to upper-right for each of doubly charged final states because of the relation: $h\nu - (KE_1 + KE_2) = BE(N_2^+)$ as mentioned above. The bottom and left panels show the projections of the correlation maps on each axis. In the bottom panels, the resonant Auger spectra (blue curves) obtained from the total measured electron yield are also plotted for comparison. The resonant Auger spectra agree well with the previously measured ones³⁻⁵ if we take into account the present energy resolution. The most prominent features on the energy correlation maps are the enhancements seen in the range $KE_2 < 2$ eV. The slow electron spectra on the left show that these enhancements consist of several sharp peaks. The positions of the peaks agree well with the kinetic energies of electrons emitted in the autoionizations of superexcited neutral N^* atoms converging to $N^+(2s^2 2p^2, ^1D^e)$ ¹⁶. The superexcited fragments are formed in the cascade RDA processes: the first step molecular Auger ($N_2 \rightarrow N_2^{*+} + e^-(KE_1)$) followed by dissociation of the molecular ion ($N_2^{*+} \rightarrow N^* + N^+$). While essentially the same autoionization peaks were observed by high-resolution electron spectroscopy⁶, high- n superexcited states, such as $N(2s^2 2p^2(^1D^e)6s)$ at $KE_2 = 1.3$ eV and $N(2s^2 2p^2(^1D^e)7s)$ at $KE_2 = 1.5$ eV, are more clearly observed in the present study. The appearance of higher member despite lower energy resolution in the present study is probably due to the elimination of unwanted background from the other processes by the coincidence measurements.

Though the slow electron spectra in the left panels gradually decrease in intensity with increasing kinetic energy, the features apparently deviate from the ordinary U-shaped distribution (see figure 3 and corresponding text). The enhancements in the low kinetic energy range are attributed to the cascade RDA processes. They are more enhanced for the core-to-Rydberg excitations ($3s\sigma$ and $3p\pi$). Red bars in the left panels indicate the energy locations of the N^+ excited states with respect to its

ground state listed in table 1. Neutral superexcited states converging to these N^+ states are expected to lie below the energy locations indicated. For the π^* excited state, spectral feature ascribable to N^* fragment is not so strong in the range $KE_2 > 2$ eV as compared with those for the Rydberg core-excited states where step-like structures are more clearly seen at, for example, $KE_2 = 5.8$ and 11.44 eV, which correspond to the $N^+(2s2p^3, {}^5S^o)$ and $N^+(2s2p^3, {}^3D^o)$ convergence limit, respectively. This observation implies that N^* fragment converging to these N^+ limits were produced in the cascade RDA decays from the Rydberg excited states. Lack of sharp peaks in the higher kinetic energy range ($KE_2 > 2$ eV) is at least partly due to low energy resolution and high density of states. It thus turns out that the π^* excited state is likely to form superexcited N^* states built on the $2s^22p^2$ ionic cores while the Rydberg ($3s\sigma$, $3p\pi$) excited states lead to the formation of superexcited states built on the $2s2p^3$ ionic cores as well. Broad molecular-Auger peaks due to competition between the bond dissociation and electron emission^{1, 18} might also be involved in the cascade contributions.

The difference in the slow electron spectra between the π^* and Rydberg excited states stems from the first step Auger decay in the cascade RDA processes. The black solid curves with shaded area in the bottom panels of figures 2(a) – 2(c) obtained by the projections of the energy correlation maps show that the processes producing the N^* fragments are associated with the molecular-ion states lying around $BE[N_2^+] \sim 47$ eV for the π^* excited states while those lying around $BE[N_2^+] \sim 60$ eV contribute largely to the N^* formations for the Rydberg core-excited states. Referring to the assignments for the conventional Auger spectra¹⁹ these ion states relevant to the N^* formations are attributed to the $(iv)^{-1}(ov)^{-1}n\lambda$ singly charged states, where iv and ov denote the inner-valence and outer-valence orbitals and $n\lambda$ is the excited orbital to which a core electron is initially promoted by soft X-ray absorption. Such singly excited states can be formed by the spectator Auger processes in which the promoted electrons remain in the excited orbital through the first step Auger transitions. The electron in the excited orbital is likely to remain further in the subsequent dissociations of the singly-charged states, leading to different N^* formations between the π^* and Rydberg excited states.

In figures 3(a) – 3(c), the kinetic energy spectra of the slow electrons in the RDA processes shown in the left panels of figures 2(a) – 2(c) are displayed over a wider energy range, where red curves with shaded area indicate results of a fitting by an exponential function to the experimental distribution above 20 eV. As mentioned before, the direct processes result in the U-shaped energy distributions while distributions concentrated in the low energy range on top of them are due to the cascade processes. While several fit functions have been proposed for the U-shaped distributions²⁰⁻²², the spectral profiles seen above a kinetic energy of 20 eV are reproduced most faithfully with exponential functions. In the present study we thus assumed that the exponential functions represent the contributions from the direct processes. By integrating the two curves in each panel on the left over the whole KE_2 range, the branching ratio between the direct and cascade processes were obtained to be 34:66, 24:76 and 23:77

for the π^* , $3s\sigma$ and $3p\pi$ core-excited states, respectively. The cascade RDA processes are more probable than the direct ones for all the core-excited states but the contribution increases with increasing excitation energy. It is known that the spectator processes are dominant in the resonant single Auger (RSA) decays from these excited states³⁻⁵ and high-lying N_2^+ states are populated more from the RSA decay from the higher core-excited state. The fraction of N_2^+ states leading to further electron emission and leading to cascade RDA processes is thus increased on the first-step Auger decay from the higher core-excited states.

The binding energy spectra of N_2^{2+} states produced in the direct RDA processes are obtained by filtering coincidence events of two electrons with $KE_2 \geq 20$ eV and plotting the histogram of the energy sums of the two electrons. They are displayed in figures 4(a) – 4(c) as a function of $BE(N_2^{2+}) = h\nu - (KE_1 + KE_2)$. In figure 4(d) the binding energy spectrum of triply charged states populated in the normal Auger decay of the core-ionized states²³ is also shown for comparison. The peaks at around 92 and 114 eV in figure 4(d) were assigned as the ov^{-3} and $iv^{-1}ov^{-2}$ triply charged states, respectively²³. Similar peak structures with shifted energy locations are found in figures 4(a) – 4(c) and they are attributed to the doubly charged states build on these triply charged ion cores, i.e. the $ov^{-3}n\ell$ and $ov^{-2}iv^{-1}n'\ell'$ states. On the other hand, the weak peak seen around $BE(N_2^{2+}) = 45$ eV is assignable to the ov^{-2} state. The $ov^{-3}n\ell$ and $ov^{-2}iv^{-1}n'\ell'$ states attained by such direct RDA are populated as the excited electron behave as a spectator while the formation of the ov^{-2} state is associated with the participation of the excited electron in the direct RDA decay. It is found that the spectator behavior is preferred for the excited electron compared to its participation in the direct RDA, in the same way as in the cascade RDA. Some of the doubly charged states populated by the spectator processes lies above the N_2^{3+} threshold (~ 84 eV²⁴) and can subsequently emit one more electron resulting in the formation of triply charged states.

3.2 Resonant Triple Auger decay

In a resonant triple Auger (RTA) processes three electrons are emitted simultaneously (direct processes) or sequentially (cascade processes)²⁵. Figures 5(a) – 5(c) represent energy correlations between the three electron coincidence events emitted in RTA decay. The horizontal axes are the difference between the photon energy and the sum of kinetic energies of the two faster electrons, $h\nu - (KE_1 + KE_2)$, which corresponds to the binding energy of intermediate doubly charged states in the cascade processes. The vertical axes are the kinetic energy of the slowest electron (KE_3). Signals of the direct processes may appear on different lines to upper-right depending on the final triply charged states ($h\nu - (KE_1 + KE_2 + KE_3) = BE(N_2^{3+})$). Projections of the coincidence counts onto each axis

are shown in the bottom and left panels. The energy correlation maps exhibit island structures located below $KE_3 = 4$ eV and the corresponding peaks appear in the slow electron spectra shown in the left panels. The positions of the peaks agree with the energies of superexcited N^+ states converging to $N^{2+}(2s2p^2, ^4P)^{17}$, which implies a presence of cascade RTA processes, i.e., $N_2^* \rightarrow N_2^{2+*} + e^-(KE_1) + e^-(KE_2)$ followed by $N_2^{2+*} \rightarrow N^{+*} + N^+$ and then by $N^{+*} \rightarrow N^{2+}(^2P) + e^-(KE_3)$. Red bars in the left panels represent the energies of the excited N^{2+} states of the doubly charged atomic nitrogen with respect to its ground state listed in table 1. Except for the $N^{2+}(2s^22p, ^4P)$ state, clear step-like structure is not discernible at the location of the other N^{2+} states, which leads that the N^{+*} fragments in the Rydberg states converging to such excited N^{2+} states are rarely produced in the cascade RTA decays. The energy correlation maps and the projection spectra on the bottom indicate that the doubly charged states around $BE(N_2^{2+}) = 100$ eV contribute to the cascade RTA processes. Following the discussion on figure 4, such N_2^{2+} states can be formed through the spectator RDA decays. Considering that the features in the slow electron spectra are similar to each other, the intermediate N_2^{2+} states relevant to the N^{+*} formation would be common among the π^* and Rydberg core-excited states.

The kinetic energy spectra of the slowest electron in the triple coincidence events are shown in figures 6(a) – 6(c). Since the energy distribution in the direct RTA process would possibly be similar to the U-shape distribution, the contribution of the direct RTA processes can also be approximated by a single exponential functions as was done for the direct RDA processes. The contributions thus estimated for the direct RTA processes are shown by red curves with shaded area in figures 6(a) – 6(c). By integrating the intensities of the two curves in each spectrum over the whole KE_3 range, the ratios of the direct RTA processes compared to the cascade processes were estimated to be 22:78, 16:84 and 13:87 for the π^* , $3s\sigma$ and $3p\pi$ excited states, respectively. The sequential ionizations are more likely than the ‘concerted’ ones as in the case of RDA and the tendency is more pronounced for the higher excited states.

3.3 Branching ratio of decays after the core excitation

The number of single, double and triple coincidence events do not directly correspond to the relative cross sections of the RSA, RDA and RTA decays because of the detection efficiency ($f = 0.5_{-0.05}^{+0.1}$) of the present measurements. Instead, relative cross sections of the RSA, RDA and RTA (I_s , I_d and I_t , respectively) were estimated for each resonant excitation from the following coupled equations:

$$\begin{aligned} I_1 &= f \times I_s + f \cdot (1 - f) \times I_d + f \cdot (1 - f)^2 \times I_t \\ I_2 &= f^2 \times I_d + f^2 \cdot (1 - f) \times I_t \end{aligned}$$

$$I_3 = f^3 \times I_t ,$$

where I_1 , I_2 and I_3 are numbers of events for single, double and triple coincidences, respectively. The obtained values are shown in table 2. The branching ratio of the RDA decays for the $1s \rightarrow \pi^*$ resonant excitation (30 ± 3) does not agree with previous value (19 ± 3) estimated by the Auger electron-ion(s) coincidence experiment⁸. In the previous measurement, Auger electrons in the limited kinetic energy range ($345 \leq KE \leq 390$ eV) were collected and as a result the contribution from the $N^{2+} + N$ decay channel (channel (5) in table 2) accompanied with the emission of Auger electron in the range $KE < 345$ eV was excluded. Indeed, if we limit the kinetic energy range as was done in Ref 8, the contribution from the RDA decays becomes 17 ± 2 which agrees with the previous measurement.

For the $1s \rightarrow \pi^*$ resonant excitation, the contribution from RDA decays is nearly half of that from RSA decays. These contributions become comparable on the Rydberg excitations. This is in clear contrast to the DA decay following K shell ionization: using a multi-electron coincidence experiment Hult Roos *et al.*²⁶ observed that more than 90 % of the core-hole state decay through SA and that only 9.4 % decay through DA. The greater probabilities for DA on the resonant excitations can be discerned by looking at the resonant Auger spectra in the bottom panels of figure 1 (blue solid curves), where considerable fractions of the distributions are above the double ionization threshold at 43 eV reflecting that it is more likely for the photoexcited electron to be a spectator. The higher core-excited states seem to have a propensity to form higher states through the single and double spectator decays resulting in emissions of more electrons as demonstrated in table 2.

While the RSA decays result in the formation of the parent N_2^+ and the $N^+ + N$ fragment pair, the RDA decays form N_2^{2+} , $N^+ + N^+$ and $N^{2+} + N$. On the other hand, since neither of N_2^{3+} nor N^{3+} were detected in the ion detection on core excitation / ionization in N_2^7 , the RTA decays result solely in the formation of $N^{2+} + N^+$. The relations between the Auger decay pathways and the product channels are summarized in first column of table 2. Considering these relations, the relative ion yields measured at the core-excited states⁷ can be expressed by the branching ratio of the decay channels. For example, the N^{2+} yield depends on the sum of the branching ratios for the product channels (5) forming $N^{2+} + N$ and (6) forming $N^{2+} + N^+$. We write this relation as $a(N^{2+}) \propto b(5) + b(6)$. Likewise following equations are deduced for the ion yields a with the branching ratios for the product channels b and for the Auger pathways c :

$$a(N_2^+) \propto b(1), \quad a(N_2^{2+}) \propto b(3), \quad a(N^+) \propto b(2) + 2b(4) + b(6), \quad a(N^{2+}) \propto b(5) + b(6), \\ c(\text{RSA}) = b(1) + b(2), \quad c(\text{RDA}) = b(3) + b(4) + b(5), \quad c(\text{RTA}) = b(6).$$

The ratios for the different Auger pathways c 's have already been obtained above and the relative ion yields a 's are available from the previous study⁷. The branching ratios obtained for the product channels are shown in table 2, which reflect dissociation dynamics in molecular ions.

The branching ratio of the N_2^+ formation in the RSA decays is much larger for the π^* excited

states than for the Rydberg excites states. A similar trend can be identified also for the N_2^{2+} formation in the RDA decays. The observation is reasonable because population of such ionic states not having internal energies sufficient for dissociation become less due to Auger decays of more-highly-excited core-hole states. It is interesting that approximately 40 % of the RDA processes result in the unbalanced-charge separation into $N^{2+} + N$ irrespective of the resonant excitations. From the discrepancy in $c(RDA)$ between the previous⁸ and the present results discussed above, such unbalanced-charge dissociation from the $1s \rightarrow \pi^*$ core-excited state would accompany the emission of Auger electron in the range $KE < 345$ eV. The correlations between the electronic relaxation processes and the ion fragmentation channels can be precisely investigated with an electron - ion coincidence technique, which was demonstrated for the single Auger decay of the $2p \rightarrow \sigma^*$ core-excited states of chlorometanes²⁷. However, it is difficult for such electron - ion coincidence measurement to gain comprehensive information of ion fragmentation after multiple Auger decays leading to complicated electron spectra. The present study demonstrates that a combination of data taken separately with electron coincidence measurements and with ion spectrometry can offer general information of ion fragmentation after multiple Auger decays.

Summary

Multiple Auger decay processes of the $1s \rightarrow \pi^*$, $3s\sigma$ and $3p\pi$ core excited states of N_2 have been investigated in detail by a multi-electron coincidence technique. All of the electrons in RSA, RDA and RTA decays originating from the core excitations were detected in coincidence. In RDA, the cascade RDA processes leading to the formation of the autoionizing neutral nitrogen atom were identified. The N^* fragments were produced by the dissociation of the singly charged molecular ions formed in the first-step spectator Auger transitions. Distributions of the doubly charged final states in the direct RDA decays were also derived. In the RTA decays, the cascade processes forming the autoionizing singly charged atomic ions were observed for all of the core-excited states. The doubly charged intermediate states producing N^{++} fragments were found to be those with the binding energies of approximately 100 eV, irrespective of the primary core excitations and produced through the spectator double Auger transitions. The branching ratios between the RSA, RDA and RTA and the ratios between the cascade and direct processes in the RDA and RTA were obtained. With the information of the ion products at the resonant excitations⁷, the branching ratios of all decay channels were determined.

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Table1

Table 1. Energies of lower excited states in singly and doubly charged atomic nitrogen measured from their ground states¹⁷.

states	Energy / eV
$N^+ (2s^2 2p^2, {}^3P_0)$	0
$N^+ (2s^2 2p^2, {}^1D)$	1.90
$N^+ (2s^2 2p^2, {}^1S)$	4.05
$N^+ (2s 2p^3, {}^5S^o)$	5.80
$N^+ (2s 2p^3, {}^3D^o)$	11.4
$N^+ (2s 2p^3, {}^3P^o)$	13.5
$N^+ (2s 2p^3, {}^1D^o)$	17.9
$N^{2+} (2s^2 2p, {}^2P^o)$	0
$N^{2+} (2s 2p^2, {}^4P)$	7.10
$N^{2+} (2s 2p^2, {}^2D)$	12.5
$N^{2+} (2s 2p^2, {}^2S)$	16.2
$N^{2+} (2s 2p^2, {}^2P)$	18.1

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Table2

Table 2. Branching ratios of Auger decay pathways from the core-excited states investigated.

Decay channels	π^*	$3s\sigma$	$3p\pi$
RSA	67 ± 4	46 ± 4	48 ± 4
(1) N_2^+	10	2	1
(2) $N^+ + N$	57	44	46
RDA	30 ± 3	48 ± 3	47 ± 3
(3) N_2^{2+}	5	3	2
(4) $N^+ + N^+$	15	24	26
(5) $N^{2+} + N$	11	21	19
RTA	3 ± 1	5 ± 1	6 ± 1
(6) $N^2 + N^+$	3	5	6

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Figure1

Figure 1. Photoabsorption spectrum of N₂ taken by plotting total electron yields as a function of photon energy. The arrows indicate the locations where the present coincidence measurements were done.

Figure2

Figure 2. Energy correlation maps between two electrons in the RDA decays from the $1s \rightarrow \pi^*$ (a), the $1s \rightarrow 3s\sigma$ (b) and the $1s \rightarrow 3p\pi$ (c) excited states of N_2 . The vertical axes are kinetic energy of the slow electron. The horizontal axes are binding energy of N_2^+ obtained by subtracting kinetic energy of fast electron from the photon energy (see text). The bottom and left panels of each figure represent the projections of the coincidence counts on the correlation maps onto the axes (black solid curves in the left and black solid curves with shaded area in the bottom). Blue solid curves in the bottom panels are the resonant Auger spectra whose intensities are normalized to the black curves at 60 eV. Red bars in the left panels represent the energies of excited states of N^+ listed in table 1. Red curves with shaded area in the left panels are contribution from the direct RDA processes (see text and Fig. 3).

Figure 3

Figure 3. Kinetic energy spectra of the slow electrons in the RDA processes from the $1s \rightarrow \pi^*$ (a), the $1s \rightarrow 3s\sigma$ (b) and the $1s \rightarrow 3p\pi$ (c) core-excited states of N_2 . Red solid curves with shaded area represent contributions from the direct RDA processes (see text).

Figure4

Figure 4. Distributions of final doubly charged states in the direct RDA decays from the $1s \rightarrow \pi^*$ (a), the $1s \rightarrow 3s\sigma$ (b) and the $1s \rightarrow 3p\pi$ (c) core-excited states of N_2 . Distributions of final triply charged states in direct double Auger decay of the $1s^{-1}$ core-hole state of N_2 measured at the photon energy of 510.2 eV^{23} is shown in (d). Black solid and dashed lines are eye guide showing convergences of the N_2^{2+} structures towards the relevant N_2^{3+} structures formed from the core-ionized state. Curves with shaded area in (a) – (c) are binding energy spectra of N_2^{2+} in RTA processes shown in bottom panels of figures 5(a) – 5(c) of which intensities are normalized at 120 eV .

Figure 5

Figure 5. Energy correlation maps between three electrons emitted in the RTA decays from the $1s \rightarrow \pi^*$ (a), the $1s \rightarrow 3s\sigma$ (b) and the $1s \rightarrow 3p\pi$ (c) core-excited states of N_2 . The vertical axes are kinetic energy of the slowest electron. The horizontal axes are binding energy of N_2^{2+} obtained by subtracting the sum of kinetic energies of faster two electrons from the photon energy (see text). Solid curves in the bottom and left panels of each figure are the projections of the coincidence counts on the energy correlation maps onto the axes. The events in the binding energy (horizontal axis) range below 75 eV are due to false coincidences and thus are excluded from the projections onto the vertical axes. Vertical bars in the bottom panels indicate the triple ionization threshold of N_2 ($\sim 84\text{eV}^{24}$). Red bars in the left panels represent the energies of excited states of N^{2+} ¹⁷ listed in table 1. Red curves with shaded area in the left panels represent contributions from the direct RTA processes (see text and Fig. 6).

Figure 6

Figure 6. Kinetic energy spectra of the slowest electrons emitted in the RTA decays from the $1s \rightarrow \pi^*$ (a), the $1s \rightarrow 3s\sigma$ (b) and the $1s \rightarrow 3p\pi$ (c) core-excited states of N_2 . Red solid curves with shaded area represent contributions from the direct RTA processes (see text).

Counts

Kinetic energy of slowest electron (eV)