# Experimental Realization of Auger Decay in the Field of a Positive Elementary Charge

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Auger electron spectroscopy is an omnipresent experimental tool in many fields of fundamental research and applied science. The determination of the kinetic energies of the Auger electrons yields information about the element emitting the electron and its chemical environment at the time of emission. Here, we present an experimental approach to determine Auger spectra for emitter sites in the vicinity of a positive elementary charge based on electron-electron-electron and electron-electron-photon coincidence spectroscopy. We observe a characteristic redshift of the Auger spectrum caused by the Coulomb interaction with the charged environment. Our results are relevant for the interpretation of Auger spectra of extended systems like large molecules, clusters, liquids, and solids, in particular in high-intensity radiation fields which are nowadays routinely available, e.g., at x-ray free-electron laser facilities. The effect has been widely ignored in the literature so far, and some interpretations of Auger spectra from clusters might need to be revisited.

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Auger decay, which is the emission of an electron upon filling an inner-shell vacancy by another electron, is a universal phenomenon and is used widely in both fundamental research as well as applied science. It was first mentioned by Meitner [1] and independently discussed and investigated by Auger [2] already in the 1920s. The kinetic energies of the emitted electrons, the so-called Auger spectrum, is a characteristic fingerprint of the emitting element, of its initial and final states, and, in molecules, clusters, liquids, and solids, of its chemical environment. Having an inherent lifetime typically in the femtosecond time range, Auger decay can serve as a natural reference clock for other ultrafast processes, e.g., molecular dissociation [3,4] or charge delocalization [5].

With the advent and establishment of x-ray free-electron lasers (XFELs) it has become possible to expose matter to high-intensity short-wavelength radiation. At very high intensities, many photons can be absorbed from a single pulse and may initiate several ionization events, either at the same site or at different sites of an extended system like large molecules, clusters, or nanoparticles. The interaction of high-intensity x-ray pulses with clusters has been studied in pioneering theoretical and experimental studies, addressing collective phenomena like nanoplasma formation, field ionization, charge migration and recombination, and their impact on nuclear dynamics and Coulomb explosion [6–12]. In a sequence of ionization events, it is obvious that all but the first one are strongly influenced by the preceding processes. For a detailed understanding of the physics governing multiple ionization due to x-ray irradiation, it is instructive to investigate the properties of fundamental mechanisms, such as Auger decay, if the decaying atom is placed in a charged environment. Theoretical studies predict significant quantitative changes in the Auger rates due to orbital distortions [13] and suppression of the exponential decay behavior by trapping of the emitted electrons [14]. Despite its importance for a comprehensive understanding and adequate modeling of the interaction of high-intensity x rays with matter, an experimental scheme for the controlled investigation of atomic decays in the field of charges at a defined distance has not yet been realized. In the present study, we report the experimental investigation of a specific Auger decay in the field of a single elementary charge.

For a comparison of the undisturbed Auger spectrum with the corresponding spectrum in the field of an elementary charge, we study the decay of an inner-shell vacancy in atomic Van der Waals clusters. With a certain probability, the outgoing inner-shell photoelectron may scatter on its pathway through the cluster and create another ion by photoelectron-impact ionization at a distance $R$ from the initial photoionization site. Since the distance between the atoms in Van der Waals clusters is large compared to the classical atomic radii, the second ion can be treated as an

 

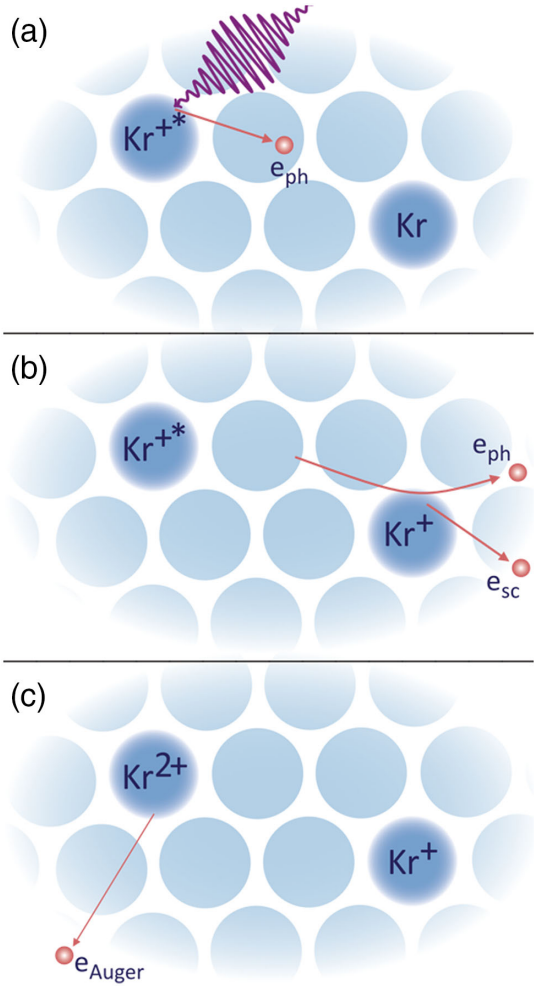


FIG. 1. Sketch of the process under investigation. (a) A Kr atom in a cluster is photoionized in the $3d$ orbital. (b) On its way through the cluster, the photoelectron scatters inelastically at another atom and ionizes it. (c) The initially ionized atom decays by Auger electron emission.

elementary point charge from the viewpoint of the excited atom. Experimentally, this specific scenario is identified by the coincident detection of three electrons: the scattered photoelectron $e_{\mathrm{ph}}$, the electron knocked out in the scattering event $e_{\mathrm{sc}}$, and the Auger electron $e_{\mathrm{Auger}}$. The three steps leading to emission of the three electrons are illustrated in Fig. 1 for the chosen example of photoionization of the $3d$ orbital in Kr clusters. First, a $3d$ electron is photoionized [Fig. 1(a)]. On its way through the cluster, it may scatter inelastically at another Kr atom, eventually ionizing it [Fig. 1(b)]. At typical excess energies, the impact ionization happens fast compared to the Auger decay [15]. The latter then takes place in the field of a neighboring positive charge [Fig. 1(c)].

The experiment was performed at the PLÉIADES beam line of the synchrotron SOLEIL in France, operated in single-bunch mode (1181 ns spacing between two consecutive photon pulses). Linear horizontally polarized soft x-ray photons of $h\nu = 127$ eV photon energy were produced by the HU 80 undulator and monochromatized by the beam line's plane grating monochromator. The experimental setup consisted of a magnetic bottle time-of-flight electron spectrometer (MBES) and a mirror assembly for efficient photon detection, following the principle of a setup developed recently for electron-photon coincidence spectroscopy [16]. In this new version, however, the HERMES spectrometer with longer drift tube and a somewhat higher energy resolution was used [17,18]. The mirror assembly was size adapted. The coincident detection enables the selection of specific decay cascades and the correlation of all particles emitted in a certain pathway. See the Supplemental Material for more details [15].

Kr clusters were produced by supersonic expansion of Kr gas at 2.5 bar stagnation pressure and room temperature through a conical nozzle of 60 μm diameter and 30° full opening angle. According to conventional scaling laws [19], these conditions result in a cluster-size distribution with a mean size of $\langle N \rangle = 60$ atoms per cluster. After passing a 0.3 mm diameter skimmer, the target jet was crossed with the synchrotron radiation. For low stagnation pressures behind the nozzle or detuned nozzle with respect to the skimmer, no clusters arrive at the interaction volume and reference spectra with gas jets containing only isolated atoms can be recorded.

For operation of both the cluster source and the MBES in the horizontal plane, they were operated in 90° with respect to each other but in 45° with respect to the synchrotron radiation. The photons were detected in the vertical direction with the detector on top of the chamber. A microchannel-plate single-photon counting detector with a CsTe photocathode was used [20]. See the Supplemental Material for a 3D schematic of the experimental setup [15].

For the validation of the proposed scheme and the interpretation of the experimental observations, it is instructive to consider the implications of the adjacent charge on the Auger decay. While the above-mentioned changes in stationary or time-resolved decay rates [13,14] are not directly accessible in the present experiment, already the mere Coulomb field will cause a shift of the Auger transition energies. The Coulomb energy $E_C$ of two charges $q_1$, $q_2$ at a distance $R$ is given by

$$E_C = \frac{q_1 q_2}{4\pi\varepsilon_0 R}, \tag{1}$$

with the vacuum permittivity $\varepsilon_0$. After the creation of the second ion by electron-impact ionization but before the Auger decay, both ions are singly charged, i.e., $q_1 = q_2 = e$, with the elementary charge $e$. Because of the large mass of the ions, any nuclear dynamics is negligible within the core-hole lifetime of 7.5 fs [21]. It can thus be assumed that the Auger decay of the initially inner-shell-ionized atom happens at the same nuclear geometry as the photoelectron-impact ionization. The decay changes the

charge of the first ion from $+e$ to $+2e$ and, consequently, doubles $E_C$. It is therefore straightforward that the Auger spectrum in the vicinity of a charge is redshifted compared to the conventional Auger spectrum by just $E_C$. $E_C$ is experimentally accessible by the determination of the kinetic energies of $e_{\mathrm{ph}}$ and $e_{\mathrm{sc}}$ and their comparison to the respective electron binding energies in Kr. We obtain an average of $E_C = 2$ eV, corresponding to a mean distance of electron-impact ionization of $R = 7.2$ Å, which is a little bit less than double the equilibrium internuclear distance in Kr clusters [22,23]. For a detailed calculation, see Ref. [15].

For an accurate experimental determination of the expected redshift of the Auger spectrum, we focus on the main decay channel of the $3d$ vacancy, in which a $4p$ electron fills the hole and another $4p$ electron is ejected, leading finally to $\mathrm{Kr}^{2+}(4p^{-2})$ states. Three total configurations with ${}^3P_{0,1,2}$, ${}^1D_2$, and ${}^1S_0$ terms contribute [24–26]. As the present experimental scenario requires the detection of scattered photoelectrons down to zero kinetic energy, the absolute resolution of the spectrometer is not sufficient to resolve the individual states of the Auger spectrum [15]. The general experimental Auger spectrum is thus a superposition of atomic, surface, and bulk contributions of both Kr $3d$ fine-structure components, which can in principle all be separated if retardation voltages are applied [27].

An Auger spectrum of isolated atoms is not appropriate for a comparison, since it is known that the Auger spectrum of clusters is shifted compared to the atomic counterpart due to polarization screening in the final states [28]. Also, a comparison to literature spectra is prone to uncertainties because Auger energies may slightly shift as a function of the exact target composition and, additionally, calibration uncertainties need to be well characterized. Therefore, as a reference for the decay in the field of a charge, an undisturbed Auger spectrum originating from the decay in clusters only ("cluster-pure Auger spectrum") needs to be measured in the same experiment. If, as in the present case, the cluster reference spectrum cannot be separated using the photoelectron coincidence spectra (as, e.g., in Ref. [27]), to our knowledge, the only way to obtain cluster-pure Auger spectra in coincidence with slow electrons is to make use of electron-electron-photon coincidences. The doubly charged Auger final states of clusters are subject to radiative charge transfer (RCT) [29–31]. In this mechanism, an electron from a neutral neighbor fills one of the two valence vacancies, and the energy released by this charge separation is emitted as a photon. Obviously, isolated atoms cannot undergo RCT. It was demonstrated recently that using UV-photon-photoelectron coincidences allows for an efficient elimination of the atomic contribution from the Auger spectra [15,32].

Figure 2 presents the main results of the present study. Auger spectra for three different coincidence conditions are presented. Black triangles represent the Auger spectrum obtained from electron-electron coincidences with the slower electron being the unscattered photoelectron, integrated over clusters and atoms as well as both fine-structure components. The red dotted line is the cluster-pure Auger spectrum, obtained from electron-electron-photon triple coincidences, with the slower of both electrons again being an unscattered photoelectron. As expected, the elimination of the atomic contribution results in an effective shift of the spectrum to higher kinetic energies [28]. Finally, the blue solid trace shows the Auger spectrum of $\mathrm{Kr}^{+}(3d^{-1})$ ions in the neighborhood of a positive charge, corrected for a linear background. It results from triple-electron coincidences of the scattered photoelectron, the knocked-out electron, and the Auger electron. See Ref. [15] for detailed information on the selected coincidence conditions and data analysis. For an easier comparison all spectra are normalized to have the same area. The maximum of the Auger spectrum of decaying ions in the vicinity of a charge is indeed redshifted by the expected value of about 2 eV compared to the conventional cluster-pure Auger spectrum, confirming the validity of our model.

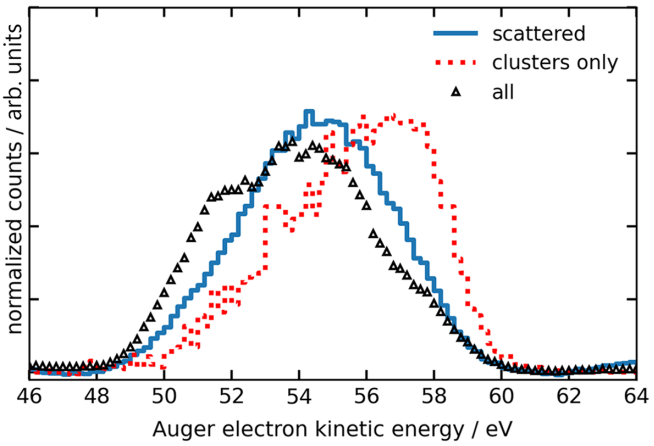


FIG. 2. $\mathrm{Kr}^{+}(3d^{-1}) \rightarrow \mathrm{Kr}^{2+}(4p^{-2}) + e_{\mathrm{Auger}}$ Auger spectra selected for different scenarios. All coincidences with unscattered Kr $3d$ photoelectrons from both clusters and free atoms (black triangles), coincidences with unscattered Kr $3d$ photoelectrons and a UV photon (red dotted line), and coincidences with the scattered photoelectrons (blue solid line; see Ref. [15] for details). The curves were background corrected and area normalized for better comparison. Before normalization, the number of counts in the peak maxima are 38 800 (all), 7700 (scattered), and 160 (clusters only). From that we estimate statistical $1\sigma$ uncertainties of 0.5%, 1%, and 8%, respectively.

For a quantitative estimate of the significance of the effect, we calculated the necessary path lengths $d_p$ of the electron trajectory in the cluster to have a 50% ($d_{50}$) or 95% ($d_{95}$) probability for causing an electron-impact ionization using the Beer-Lambert law and tabulated electron-impact-ionization cross sections. We obtain $d_{50} = 1.0$ nm and $d_{95} = 4.2$ nm for Kr at 65 eV electron kinetic energy. Although approximated, these numbers agree well with the obtained average impact-ionization

distance of 7.2 Å from the present data as well as with measurements of the mean free path of electrons in rare-gas clusters [33]. A detailed description of the model and a table providing values of $d_{50}$ and $d_{95}$ for all rare gases can be found in the Supplemental Material [15], including the input parameters [34,35]. These estimates show that the described phenomenon can easily reach significance for clusters in the size range of few nanometers and even below.

It is worth mentioning that another important phenomenon affecting the kinetic energy of Auger electrons is postcollision interaction (PCI). As discussed above, Auger decay is mostly regarded to be independent of the initial ionization process and the fate of the photoelectron. Only if the excess energy of the photoelectron is so low that it still feels a strong Coulomb potential of the ion when the Auger electron is emitted, both electrons can interact through PCI [36–39]. Simplified, this can be regarded as a classical overtaking process: the Auger electron overtakes the photoelectron. From the perspective of the electrons, the charge state of the ion changes at the moment of overtaking. This results in energy exchange: the overtaking Auger electron becomes faster while the overtaken photoelectron is decelerated. If the effect is strong, the photoelectron may even be recaptured by the ion [40–43]. PCI and recapture serve as prototype processes for electron correlation and have been studied extensively. In the present study, we show that through interaction with the environment Auger decay can be influenced significantly by the fate of the photoelectron even for high excess energies.

We experimentally verified and investigated a fundamental shift in the kinetic energy of Auger electrons emitted from excited atoms in the vicinity of a positive charge. The observed shift agrees with an estimate of the Coulomb energy, which needs to be considered due to the change in charge state of the decaying atom. Our results are relevant for various scenarios in which Auger spectroscopy is applied and will open new perspectives.

We propose that the effect distorts all Auger spectra of clusters, if they were not measured in coincidence with (unscattered) photoelectrons and the excess energy exceeds the impact-ionization threshold. In a conventional Auger electron spectroscopy experiment on clusters, it is highly nontrivial and typically not implemented to track the fate of the photoelectron. This means that most noncoincident Auger spectra in the literature are a superposition of the undisturbed Auger spectrum and the Auger spectrum in the field of a charge, with the ratio of those two cases depending on the size of the clusters and the photoelectron excess energy. Some Auger studies may be revisited taking into account the results of the present study.

We emphasize that the presented scheme can be transferred to a variety of other scenarios. Higher charges can be involved even if the ionization is triggered by single-photon excitation. For example, the photoelectron may scatter twice or more often and produce several ions at different locations, if its excess energy suffices. For clusters above a certain size, this seems actually quite likely. Also, the impact ionization can directly produce dications by electron-impact double ionization. For Kr, e.g., the ratio of double to single electron-impact ionization is about 7%, thus significant, once the excess energy has passed the double-ionization threshold [44].

While the presence of a charge significantly influences the kinetic energy of emitted fast secondary (Auger) electrons, as in the present case, the impact could be more drastic in the case of emission of very slow electrons close to zero kinetic energy, as it is common for nonlocal autoionization like interatomic Coulombic decay [45] or electron-transfer-mediated decay [46]. Here, the additional Coulomb energy could fully close the decay channel. This will be subject to future research.

In XFEL experiments on clusters and nanoparticles, the effect is expected to be omnipresent whenever the intensity is high enough to cause several ionization events in a single particle by a single photon pulse. Importantly, the magnitude of the effect will scale with the number of charges created. It is thus evident that present charges need to be considered for the interpretation of any secondary-electron spectra resulting from high-intensity light-matter interaction.

We envision that also the fundamentals of radiative or radiationless decay of excited atoms in disturbed potentials may be explored. The adjacent charge distorts the spherical atomic potential, leading to, e.g., the above-mentioned variations of Auger decay rates [13]. In a follow-up experiment, the scheme may be changed to observe not only a single Auger transition but a number of transitions into different final states. By carefully investigating the branching ratios, relative transition probabilities can be probed. An influence on the selection rules for radiative decay is also conceivable. The predicted suppression of the exponential decay behavior of Auger decay [14] is experimentally more challenging to realize, since it requires soft x-ray pump-probe experiments using electron-electron coincidences. Such techniques are, however, not out of reach for modern XFEL facilities which aim at high-repetition operation modes enabling covariant electron detection.

Finally, we note that it is intuitive to assume a positive correlation between the sum of the kinetic energies of the scattered photoelectron and the knocked-out electron, and the kinetic energy of the Auger electron, since both are essentially determined by $R$. That means a higher kinetic energy of the former should correspond to a higher kinetic energy of the latter, enabling a distance-dependent study of the effect. This correlation is, however, not resolvable in the present case, and moreover canceled out by the fine-structure splitting [15]. It should be subject to further investigations.

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