



## Correlated Electron Dynamics at Surfaces Investigated via $\text{He}^{2+}$ Ion Neutralization

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The neutralization of a single  $\text{He}^{2+}$  ion near a Ir surface leads to the emission of an electron pair. Via coincidence spectroscopy we give evidence that a sizable amount of these electron pairs originate from a correlated single step neutralization of the ion involving a total of four electrons from the metal. These correlated electron pairs cannot be explained in the common picture of two consecutive and independent neutralization steps. We infer a characteristic time scale for the correlated electron dynamics in the metal of 40–400 as.

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Early in the 20th century it was established that elements in the gas phase emitted light with well-defined frequencies; e.g., the hydrogen spectrum followed Balmer's law [1]. A first explanation was Bohr's postulates. Electrons occupy stable orbits with well-defined energies [2]. A transition between orbits of different energies is possible via emission or absorption of light.

Auger discovered that sufficiently energetic radiation which removes an electron from a lower level is accompanied by the emission of a second electron. This is a radiationless transfer of energy gained by the rearrangement of electrons [3,4]. The Auger effect is a double ionization process in which a single photon removes two electrons from matter.

The simplest system displaying double ionization is the He atom if the energy exceeds the double ionization energy,  $\text{DI} = 79.01$  eV. The energy in excess of this threshold is carried away by the two liberated electrons. The energy sum of these two electrons is fixed due to energy conservation, but it is continuously shared among them [5,6]. A  $\text{He}^{2+}$  ion can also be generated by the sequential absorption of two photons if they exceed the first and second ionization energy of 24.59 and 54.42 eV, respectively. In contrast to single-photon ionization, the emitted electrons now carry well-defined energies while possessing an energy sum determined by energy conservation.

The availability of intense and short light pulses has opened up new and active research fields. This allows us to address fundamental questions on the time evolution of the electron dynamics leading to electron emission [7–10]. For example, if two photons in close temporal proximity excite a sample, will the system react as if two independent energy quanta are donated, or does it recognize the two photons as one energy quantum? Theory answered this for two-photon double ionization of He via an intense photon beam with 70 eV photons [11,12]. A single photon cannot create a  $\text{He}^{2+}$  ion, only the absorption of at least two photons can achieve this. If the temporal width of the beam is below 300 as, most of the two emitted electrons share the available

energy continuously. Hence, the system responds as if one energy quantum of 140 eV is absorbed. Pulse widths larger than 4.5 fs lead to electron emission with well-defined energies indicative of two sequential ionization steps. Such studies hold the promise to determine the time scale  $\tau$  for correlated electron dynamics.

We describe an experiment on a solid surface using an alternative route. It is based on the reversed process of ionization called neutralization near a surface. This effect takes place at about 2–6 Å from the surface and causes electron emission via a radiationless transfer of energy [13–21]. A proper description requires us to include the  $d$  electrons of the surface electronic structure [17,18]. It is an efficient process, because almost all incoming  $\text{He}^{2+}$  ions leave the surface region as atoms [13–15]. Transition rates for  $\text{He}^{2+}$  neutralization are known [19–21] and correspond to an average time of 2–20 fs between the two neutralization steps. This means there is a finite probability for two energy quanta to become available covering the interesting range of 300 as to 4.5 fs.

Via coincidence electron spectroscopy we provide the first direct evidence that the neutralization of a single  $\text{He}^{2+}$  ion leads to electron pair emission. We identify events where the double ionization energy is fully available. Among them we observe pairs where both electrons have the same kinetic energy. In this case the temporal separation between the two ionization steps must be shorter than the time scale  $\tau$  of correlated electron emission. From our data we estimate for  $\tau = 40$ –400 as.

In Fig. 1 we show one particular neutralization path for a singly charged ion leading to electron emission. As the ion approaches the metal surface the atomic energy levels are slightly bent upwards due to the image charge of the ion; this shift is about 2 eV [14,18]. Eventually a metal electron makes a transition into a projectile level. The energy gain is transferred radiationless to another metal electron. If it is energetically possible, electron emission sets in. This scenario is called Auger capture. There also exist other neutralization pathways for a single charged ion. For a

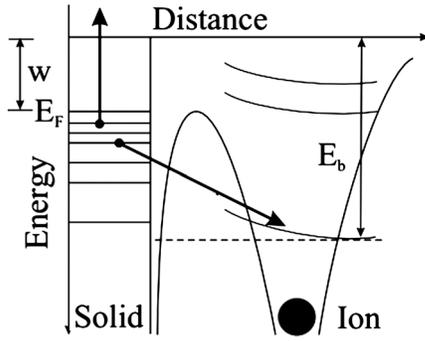


FIG. 1. Neutralization step via Auger capture.  $E_F$  ( $W$ ) denotes the Fermi level (work function) of the metal. The energy level of the projectile at infinite distance is  $E_b$ . The atomic levels are shifted close to the surface due to the image charge. A metal electron makes a transition into the lower lying level of the ion leading to electron emission from the metal.

doubly charged He ion a sequence of different paths leads to a neutral atom [19,20]. For low kinetic energy He ions the kinetic energy can be ignored in the energy balance [22]. The neutralization step from  $\text{He}^{2+} \rightarrow \text{He}^+$  and subsequent electron emission can be written as



In this process the metal  $M$  loses two electrons. One changes the charge state of the ion and one is emitted. Let us ignore the atomic level shift for the moment. Then the highest energy of the emitted electron is the ionization energy 54.42 eV minus twice the work function. The work function for Ir(100) is 5.76 eV; therefore, an electron emitted from this surface has a maximum energy of 42.9 eV. In analogy, we write for the neutralization step from  $\text{He}^+ \rightarrow \text{He}^0$ :



Again the surface donates two electrons, one of which is ejected into the vacuum. The maximum energy of this electron is the ionization energy 24.59 eV minus twice the work function, which yields 13.07 eV Ir(100). After the neutralization of  $\text{He}^{2+} \rightarrow \text{He}^0$ , the energy sum of the two emitted electrons has an upper bound defined as  $E_{\text{sum}}^{\text{max}} = DI - 4 \times W$ ; the factor 4 is a consequence of the donation of four electrons from the metal surface. The numerical value of  $E_{\text{sum}}^{\text{max}}$  is 55.97 eV for Ir(100). It is possible that the neutralization does not yield the He atom in the ground state, but in its first excited state (19.82 eV above the ground state). For the low ion energies we use, this pathway can be ignored [14].

The reaction equations [Eqs. (1) and (2)] imply that each incoming He ion leads to an emission of electrons. However, total yield measurements showed that for  $\text{He}^+$  ( $\text{He}^{2+}$ ) neutralization about 0.3 (0.8) electrons are emitted per incoming ion [23,24]. This does not contradict the

statement that almost all incoming ions leave the surface as atoms. It merely reflects the fact that energy has been transferred to an electron, but it does not escape the metal, because the propagation direction is away from the surface. The question arises as to whether a single  $\text{He}^{2+}$  ion can lead to electron pair emission. This can only be answered by a coincidence experiment.

The coincidence spectrometer is described in more detail elsewhere [25,26]. It incorporates two hemispherical electron energy analyzers. We label the spectrometers as “left” and “right,” respectively. The two transfer lenses include an angle of  $90^\circ$  and define the reaction plane. The primary  $\text{He}^{2+}$  beam with energy 10 eV lies in this plane. The emitted electrons are detected with energies  $E_{\text{left}}$  and  $E_{\text{right}}$ . The normal incident  $\text{He}^{2+}$  beam was delivered by a modified ion gun and a Wien mass filter [27,28]. This suppressed the main impurity  $\text{H}_2^+$  in the beam by using  $^3\text{He}$ . The Ir(100) surface was cleaned by annealing cycles up to 1400 K in an oxygen atmosphere of  $5 \times 10^{-8}$  mbar followed by a high temperature flash up to 1600 K [29]. The spectrometer covered an energy window of  $\pm 13.5$  eV around a central energy  $E_k$ . The energy resolution was 0.7 eV per spectrometer. We employ a coincidence circuit in which the channel plate signals from the two spectrometers have to be within 150 ns.

For a valid event the arrival times ( $t_{\text{left}}$  and  $t_{\text{right}}$ ) with respect to the coincidence trigger are known. This leads to the arrival time difference  $\Delta t = t_{\text{left}} - t_{\text{right}}$  distribution. Electron pair emission upon single-particle excitation exists if it displays a peak [26]. Such a peak shows up in Fig. 2 for a Ir(100) surface excited by a 10 eV  $\text{He}^{2+}$  beam. This is the first direct proof that the neutralization of one  $\text{He}^{2+}$  ion leads to electron pair emission (*true coincidences*). The peak width reflects the time resolution of the instrument [30,31]. The constant background (*random coincidences*)

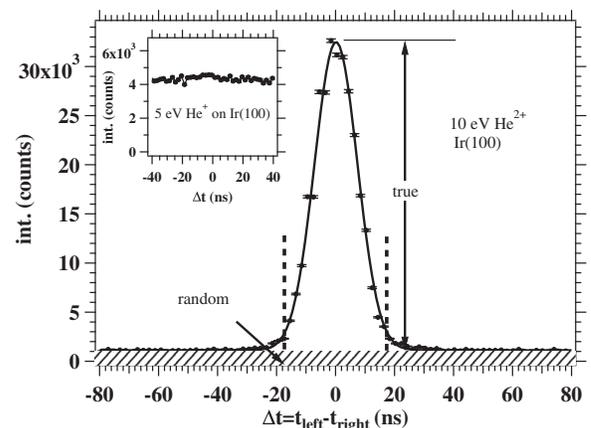


FIG. 2. Arrival time histogram of electron pairs emitted from Ir(100) due to 10 eV  $\text{He}^{2+}$  ions. The peak is indicative of “true” coincidences while the constant background arises from “random” coincidences. The dashed vertical lines indicate the selection for the energy spectra of Fig. 3. Excitation with 5 eV  $\text{He}^+$  ions showed no evidence of pair emission; see inset.

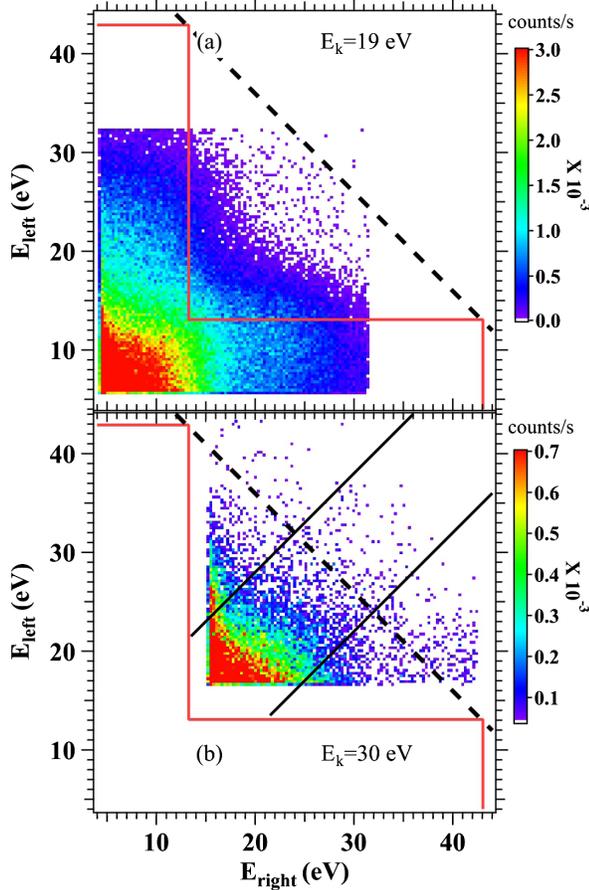


FIG. 3. 2D-energy spectra for a central energy of  $E_k = 19$  eV (a) and  $E_k = 30$  eV (b). The red lines mark an  $L$ -shaped region; events within this originate from a sequential emission. The dashed black diagonal lines mark  $E_{\text{sum}}^{\text{max}}$ . The pair of black solid lines in (b) label the region  $|E_{\text{right}} - E_{\text{left}}| \leq 8$  eV used for the  $E_{\text{sum}}$  spectrum of Fig. 4.

is due to electron emission by two  $\text{He}^{2+}$  ions. The observation of pair emission due to  $\text{He}^{2+}$  neutralization is not a trivial point. Using 5 eV  $\text{He}^+$  ions shows no evidence of pair emission, see inset of Fig. 2, while the energy gain in this neutralization (24.59 eV) would be sufficient for pair emission.

The 2D-energy spectra upon  $\text{He}^{2+}$  excitation are displayed in Fig. 3; we selected events within the interval marked by the dashed vertical lines in Fig. 2. These data were obtained for two different settings of the spectrometer. Both plots include a region bounded by red lines. Within this  $L$ -shaped region one electron can have an energy up to 42.9 eV while the other cannot exceed 13.07 eV. Therefore, this region captures events in which one electron is emitted first upon neutralization from  $\text{He}^{2+} \rightarrow \text{He}^+$  while the second is due to the neutralization from  $\text{He}^+ \rightarrow \text{He}^0$ . The dashed diagonal lines in both panels indicate the position of  $E_{\text{sum}}^{\text{max}} = 55.97$  eV of pairs.

Figure 3(a) shows the result if both spectrometers have a central energy  $E_k = 19$  eV. The highest intensity is found

if both electrons are below 10 eV. Furthermore, most of the intensity is captured by the  $L$ -shaped region. Hence, the two neutralization steps leading to  $\text{He}^0$  proceed mainly independently. A small but sizable intensity resides outside the  $L$ -shaped region, which suggests an additional pathway of pair emission. We focused on this region and changed the central energy to  $E_k = 30$  eV. Therefore, the  $L$ -shaped region is outside the field of view; see Fig. 3(b). This means we capture events that cannot be explained by a sequence of neutralization steps. The intensity is highest if both electrons have an energy at the lower part of the detection window. The intensity gradually decreases if one moves closer to the dashed diagonal line marking  $E_{\text{sum}}^{\text{max}}$ . However, a cutoff value where the intensity drops sharply cannot be identified. As a matter of fact, there is some intensity above the  $E_{\text{sum}}^{\text{max}}$  line which seems to violate energy conservation. We will show below that this intensity stems from random coincidences.

For a more detailed view we calculate for each coincidence event the energy sum  $E_{\text{left}} + E_{\text{right}}$  and plot the resulting histogram. Furthermore, we focus on events for which both electrons have similar energies. This scenario is not covered by a sequential emission. In Fig. 4(a) we present the  $E_{\text{sum}}$  energy spectrum obtained from the data set plotted in Fig. 3(b) under the constraint  $|E_{\text{right}} - E_{\text{left}}| \leq 8$  eV. For smaller differences the statistics are not sufficient for

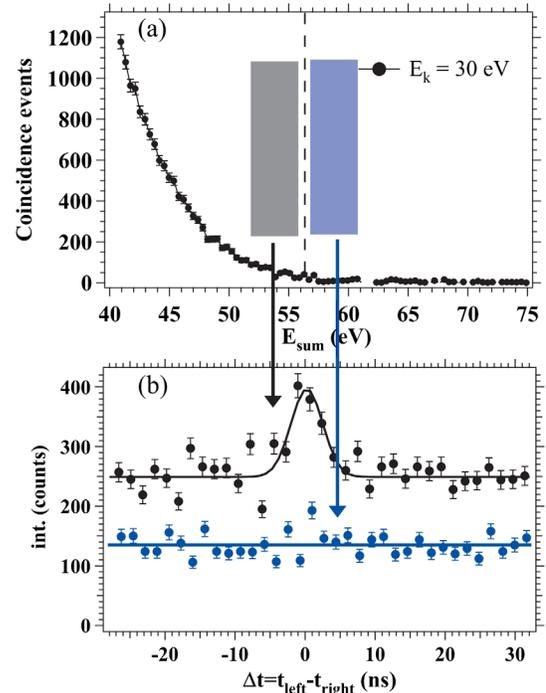


FIG. 4. Panel (a) shows the  $E_{\text{sum}}$  spectrum of the data presented in Fig. 3(b) under the constraint  $|E_{\text{right}} - E_{\text{left}}| \leq 8$  eV. The vertical dashed line marks  $E_{\text{sum}}^{\text{max}}$ . In (b) we plot the  $\Delta t$  histogram for an  $E_{\text{sum}}$  range just below or above  $E_{\text{sum}}^{\text{max}}$  as indicated by the two boxes in (a).

presentation. The pair of solid diagonal lines in Fig. 3(b) indicate this energy range. The  $E_{\text{sum}}$ -spectrum shows a monotonic decrease without a sharp cutoff near  $E_{\text{sum}}^{\text{max}}$ . This energy position is marked by the dashed vertical line.

In Fig. 4(b) we compute the  $\Delta t$  histogram for a sum energy range of width 4 eV just above or below  $E_{\text{sum}}^{\text{max}}$ . The error bars refer to the  $\sqrt{N}$  error. The selection below  $E_{\text{sum}}^{\text{max}}$  displays a peak in the histogram which proves pair emission. The constant  $\Delta t$  curve for events just above  $E_{\text{sum}}^{\text{max}}$  demonstrates the lack of pair emission. The histogram leading to a peak covers an energy range in which the cutoff lies if we consider the atomic level shift. Therefore, we cannot determine its significance for pair emission. From Fig. 4 we learn that pair emission exists in which the He atom is in the ground state. This means the full double ionization energy is available for electron pair emission. We conclude that a sequence of neutralization steps does not account for the intensity observed in Fig. 3(b).

We take a closer look at the intensity levels of Fig. 3(a). Outside the  $L$ -shaped region only 2% of the total intensity is found. With this information we propose a simple picture to estimate the time scale  $\tau$  for the correlated electron emission. The two neutralization steps occur on average within a time  $t_{\text{av}}$  and we assume that they proceed independently. The small intensity contribution outside the  $L$ -shaped region indicates that  $t_{\text{av}} \gg \tau$ . The probability for the two neutralization steps to occur within a time interval  $\tau$  is then given by the Poisson distribution  $P(\tau/t_{\text{av}}) \approx \tau/t_{\text{av}}$ . If the intensity contribution outside the  $L$ -shaped area is a measure of  $t_{\text{av}}/\tau$ , we obtain  $\tau = 0.02t_{\text{av}}$ . We adopt for  $t_{\text{av}}$  values in the range 2–20 fs on the basis of neutralization rates [19–21]. This finally yields  $\tau = 40$ –400 as. Hence, two formally independent neutralization steps occurring within an interval shorter than  $\tau$  are recognized as a single excitation for electron pair emission.

We suggest the following microscopic picture. If a core vacancy is filled by an electron, the available energy can be transferred to two electrons; see Fig. 5(a). This double Auger decay has been observed in coincidence spectroscopy from Ar [32]. Via C and N ion collisions with Ni surfaces and carbon foils, it was discovered that the electron emission spectrum also contained intensity at twice the nominal Auger electron energy of the projectile [33,34]. This was explained by a three-electron Auger decay; see Fig. 5(b). A double core hole is filled by an electron pair, and this energy is transferred to another single electron. Therefore, we interpret our data by a combination of these two processes; see Fig. 5(c). Upon approaching the surface the double vacancy of the  $\text{He}^{2+}$  ion is filled by two electrons reminiscent to the three-electron Auger. The key difference is that these electrons do not originate from higher lying orbitals of the atom, but come from the surface. The energy gain is transferred to an electron pair of the surface which is emitted. This view is further corroborated by a recent work in which the electron capture for  $\text{He}^{2+}$  ions

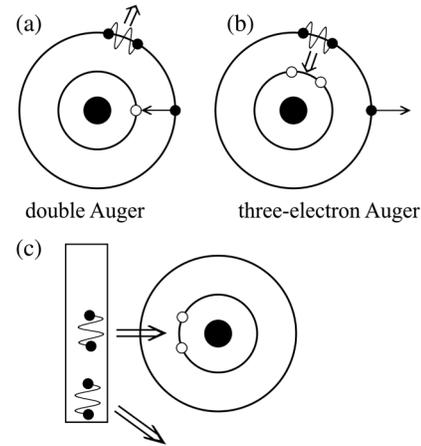


FIG. 5. In (a) a core hole is filled by an electron and pair emission called double Auger decay takes place [32]. In the three-electron Auger (b), a double vacancy is filled by an electron pair and the gained energy is transferred to a third electron [33,34]. In (c) an electron pair of the metal fills the double vacancy and an electron pair from the metal is emitted.

into excited states proceeds in a single step [28]. Extending this picture of a correlated double electron capture, we observe here a single step of an electron pair from the metal into the ground state of the He atom. If a single electron were to gain the energy of the two neutralization steps, it would have an energy up to 62 eV; this is not observed. This is consistent with our explanation of two formal neutralization steps for the pair emission.

The neutralization of a single  $\text{He}^{2+}$  ion near a metal surface leads to electron pair emission. A sizable amount of these pairs originate from a correlated single step neutralization of the ion involving a total of four electrons from the metal. On the time scale of the correlated electron dynamics, these two neutralization steps do not proceed sequentially. We infer a time scale of the correlated electron dynamics in the range 40–400 as.

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