Dynamic Screening Probed by Core-Resonant Double Photoemission from Surfaces

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The universal response of a sudden created core hole, predicted to occur on an attosecond (10^{-18} s) time scale, lacks an experimental demonstration. With a two-dimensional coincidence spectrometer, we demonstrate an extensive energy sharing between the Ag $4p$ photoelectron and the $N_{2,3}VV$ Auger electron exceeding 10 eV. This energy width provides access to the time scale of the emission process. This is the fingerprint of the dynamic fluctuation process $4p^{-1} \rightleftharpoons 4d^{-2}4f$. The shakeup induced interband transitions from the Ag(100) surface are also identified by comparing the coincidence spectrum with the $M_{4,5}VV$ Auger transitions.

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Einstein explained the photoelectric effect using the concept of quantized absorption of energy now called photons [1]. Einstein already anticipated that the energy of a single photon can be transferred to more than one electron, e.g., two electrons, in which case we may call the effect double photoemission (DPE) in one step. The simplest example of such a process is double ionization of a He atom which requires a minimum energy of 79 eV. A sufficiently energetic photon liberates the two electrons into the vacuum leaving a He^{2+} ion behind. The energy in excess of the double ionization threshold determines the energy sum of the two electrons, and it is observed that this energy is continuously shared between the electrons [2].

If a photon is absorbed by a tightly bound electron, a photoelectron is emitted with a well-defined energy characteristic for each element. The system is in an excited state and will decay in a second step via the emission of another electron, known as an Auger electron, in which two less bound electronic states are involved, e.g., the valence band [3]. The Auger electron energies are also element specific. The spectroscopy of these electrons is an important tool for the chemical analysis of surfaces. Also in this DPE process the energy sum of the emitted electrons is fixed.

These general considerations allow us to sketch the expected form of the 2D-energy distribution in a DPE experiment in which the axes represent the individual energies. A constant sum energy of a pair is defined as a diagonal line in such a distribution. The case of the Auger decay is depicted in Fig. 1(a). The intensity pockets of the Auger-photoelectron pair lie within a pair of such lines. In contrast to this Fig. 1(b) shows no preferred single electron energy. Rather, the pair is characterized by constant sum energy, while the individual electrons share this energy continuously. It is customary to convert the photoelectron linewidth Γ_1 into a lifetime via the energy-time uncertainty relation. Such an approach is not warranted in the scenario depicted in Fig. 1(b), where the intensity is found within a diagonal band. In this case the spectrum is characterized by a width Γ_2.

The observation of element-specific sharp photoelectron peaks implies the validity of the quasiparticle picture. In this case the width Γ_1 reflects the lifetime. Such a picture is known to break down for the elements ranging from Ag to Xe in the periodic table as far as the $4p$ excitation is concerned. Experimentally, rather broad $4p$ lines were observed [4].

The explantation of this fact was given by the notion of a rapid fluctuation of the $4p$ core hole to a configuration with two $4d$ holes and an electron in the $4f$ continuum [5,6]. The resulting Auger emission is known as a super Coster-Kronig transition, which is suggested to take place on a subfemtosecond time scale. A consequence of this picture is that conservation of the sum energy demands an equally broad Auger line. In other words, we have to expect an outcome as sketched in Fig. 1(b) [7].

The core hole switches on a local potential and triggers a series of dynamic electron screening processes, such as the shakeup of the outer-shell electrons, plasmon excitations,

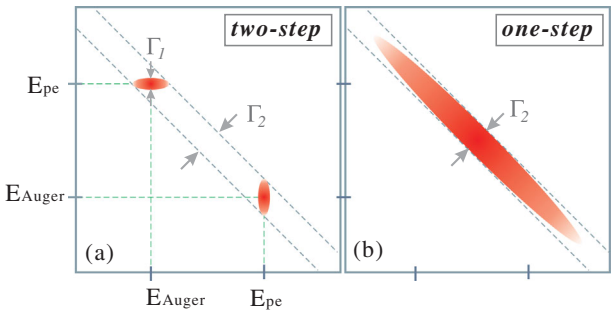

FIG. 1 (color). The schematic view of typical 2D energy distributions of DPE pairs in (a) two-step and (b) one-step picture.

and the emission of Auger electrons. This electron dynamics, unfolding on the few-femtosecond or even attosecond time scale [8,9], is accessible in principle with attosecond time-resolved spectroscopy [10,11]. A line-shape analysis of the single electron spectrum [12,13] is not applicable for the scenario sketched in Fig. 1(a)

In this Letter, we demonstrate that an extraordinarily broad photoelectron peak is in reality a sharp electron pair peak. The attosecond time scale of the emission process is accessible via the width of the energy sharing without the need of an attosecond light source. We selected Ag as a sample, because its $4p$ line deviates from the quasiparticle picture [4] and has a linewidth of 13 eV [14]. We studied the ensuing $4p\,4d\,4d$ transition and compared it with the $3d\,4d\,4d$ decay. The $3d$ line width is 0.3 eV, which is significantly smaller than the $4p$ width [15].

The experiments were performed at the undulator beam line UE56/2-PGM-2 [16] of the BESSY-II electron storage ring. Our coincidence spectrometer combines two hemispherical energy analyzers with their electron-optical axes perpendicular to each other [17]. The normal incident photon beam and the two outgoing electrons lie within the scattering plane spanned by the [001] and [100] direction of the Ag(100) surface, as shown in the inset of Fig. 2(b). Both electron's emission angles were $45° \pm 15°$ with respect to the surface normal. The pass energy and mean kinetic energy of both spectrometers were set to detect the electron pairs within a kinetic energy range of 27×27 eV^2. The energy resolution of each spectrometer was 0.8 eV. All kinetic energies are quoted with respect to the vacuum level of the clean Ag(100) surface obtained by standard sputtering-annealing cycles. All experiments were performed at room temperature. The base pressure of the chamber was 8×10^{-11} mbar.

We performed experiments at two different photon energies, 739 and 118 eV. This ensures that the two electrons forming a pair have similar energies, and the resulting 2D-energy distributions are shown in Fig. 2. With $h\nu = 739$ eV, we investigate the pair emission following the $3d$ excitation while $h\nu = 118$ eV focuses on the $4p$ decay.

In Fig. 2(a) the spin-orbit split photoelectron lines are clearly recognized at 366.6 eV ($3d_{5/2}$) and 360.9 eV ($3d_{3/2}$), respectively. Their counterparts are Auger electrons at energies of 347.3 eV (M_5VV) and 353 eV (M_4VV). The main part of the coincidence intensity lies within the pair of solid diagonal lines which mark a sum energy range centered at 713.9 eV. Clearly, we have the result expected from the sketch of Fig. 1(a).

A suitable reference energy is the photon energy minus twice the work function, called $E_{\mathrm{sum}}^{\mathrm{max}}$. This facilitates the comparison of spectra obtained with different photon energies. This energy position has been included as a dashed diagonal line in both spectra of Fig. 2. It describes the emission of two electrons from the Fermi level E_F,

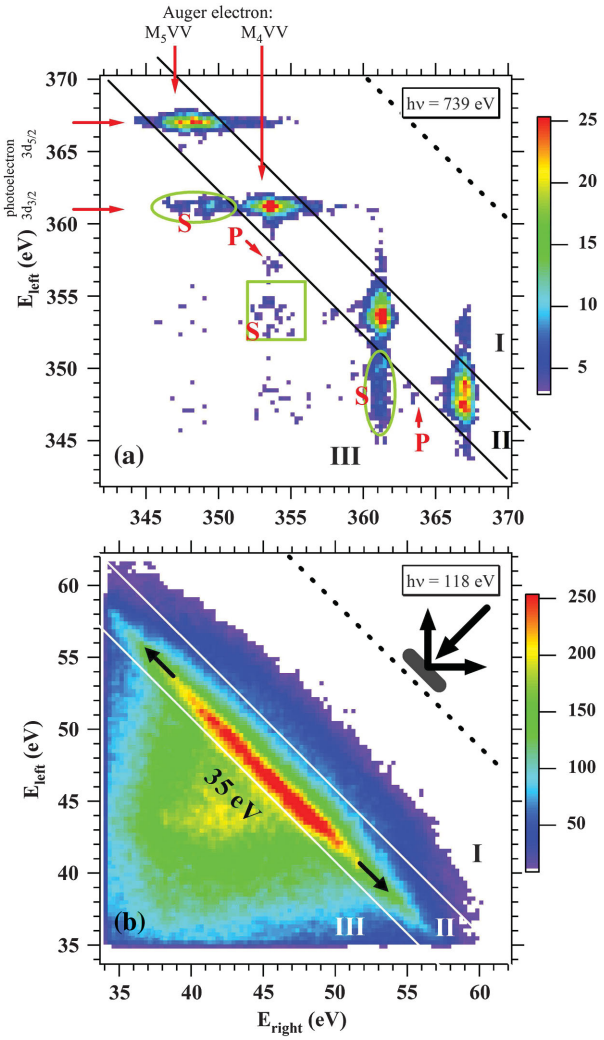

FIG. 2 (color). The 2D-energy distributions of the DPE intensity. The photon energies are in (a) 739 eV and (b) 118 eV, respectively. The dashed lines indicate the position of the maximum sum energy $E_{\mathrm{sum}}^{\mathrm{max}}$. Within the pair of solid lines most of the intensity can be found. These lines confine a sum energy range of $20 > E_{\mathrm{sum}}^{\mathrm{max}} - E_{\mathrm{sum}} > 13$ eV. The prominent intensity band in (b) has a width of 35 eV as marked by the arrows.

the numerical value is 730.3 eV for the excitation with $h\nu = 739$ eV. With this in mind we define three regions labeled as I, II, and III in Fig. 2. Region I ranges from $E_{\mathrm{sum}}^{\mathrm{max}}$ until the regime where the main part of the intensity lies, which we refer to as II. Below this energy range we find region III. This is dominated by the energy loss contributions of the DPE pairs from region II. The enhanced intensities in Fig. 2(a), as labeled by the ellipses or rectangle **S** and the arrows **P** in Fig. 2(a), are due to the elastic photoelectrons (Auger electrons) in coincidence with the corresponding inelastic Auger electrons (photoelectrons).

Figure 2(b) shows the 2D energy distribution of the DPE intensity following the $4p$ excitation. Clearly, the

intensity is dominated by a diagonal intensity band. The width of this band is 35 eV, as indicated by the black arrows. It falls energetically into a sum energy window $20 > E_{\mathrm{sum}}^{\mathrm{max}} - E_{\mathrm{sum}} > 13$ eV, that is region II. Obviously it does not make sense to speak of an Auger or photoelectron in this decay, because there is no characteristic single electron line. If the ability to detect electron pairs is not given, then the single electron spectrum [a projection of the 2D distribution Fig. 2(b) onto one axis] would appear with a width that is broader than the sum energy width Γ_2. An extraction of the lifetime from this single spectrum would be flawed.

The $N_{2,3}VV$ Auger electrons cannot be identified in conventional electron spectroscopy. It requires low-energy positron-induced Auger spectroscopy [18] or one-dimensional coincidence spectroscopy for observation [19]. Both works observed an associated prominent low-energy tail, whose origin remained unclear. This low-energy tail also has prominent intensity in region III of Fig. 2(b), and will be discussed later in the sum energy spectra.

It is appealing to compare the coincidence intensity as a function of the energy sum; see Fig. 3(a). Both spectra are presented as relative intensity, with the area of each spectrum equal to 1. Furthermore, we use as the energy scale $E_{\mathrm{sum}}^{\mathrm{max}} - E_{\mathrm{sum}}$. Despite the largely different 2D-energy spectra, the sum energy spectra are similar. In particular, the maximum intensity occurs at 16.4 eV, indicating the same Auger final state. The difference spectrum displayed in Fig. 3(b) reveals a spectral weight transfer between region II and III that is for $30 > E_{\mathrm{sum}}^{\mathrm{max}} - E_{\mathrm{sum}} > 13$ eV. In region I, both spectra overlap with each other quite well.

Region II corresponds to final states with two holes $4d^{-2}$ mainly located within the same atomic site. The strong Coulomb interactions between the two holes lead to the appearance of a well-resolved peak, which can be assigned to the atomic multiplet terms $^1G, ^3F$, etc. [21]. Thus, the electron configurations for region II can be labeled as $4d^{-2}$.

Region III covers the energy loss contributions of the DPE pairs in region II. For the $M_{4,5}VV$ pairs, the features **S** within Fig. 2(a) show up as a broad peak, labeled with **S**, in the E_{sum} spectrum. With respect to the main peak (16.4 eV) in region II, the peak **S** has energy loss around 6–8 eV, superimposed on the shoulder **P** starting with energy loss 3.7 eV. They are collective plasmon excitations, mediated by single-particle interband transitions [22,23]. In contrast, the peak **S** and shoulder **P** cannot be resolved in the $N_{2,3}VV$ E_{sum} spectrum.

The difference spectrum also reveals two peaks, centered at energy loss of 5.2 (**P1**) and 10.4 (**P2**) eV. They can be assigned to the single and double interband transition, respectively. The peak **P2** has a width of 4.8 eV, $\sqrt{2}$ times the width of the peak **P1** 3.5 eV, further manifesting itself as a double interband transition. It results from the pairing of the electron-hole pair with equal and opposite momentum due to the vacuum fluctuation, as predicted theoretically

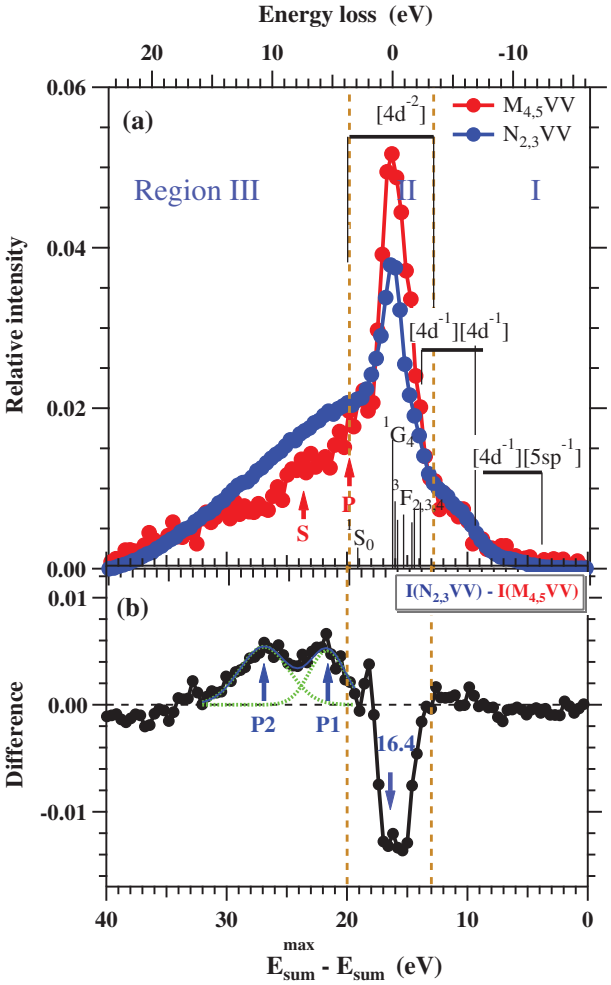

FIG. 3 (color). (a) The sum energy spectra from the $M_{4,5}VV$ (red) and the $N_{2,3}VV$ (blue) transition are shown. For this we integrated the intensity data of Fig. 2 along down-sloping diagonal lines. The intensities are normalized to the corresponding total counts. The relative intensities of the different Auger final state multiplets from theoretical atomic calculations [20] are included as vertical bars. (b) The difference spectrum between the above two sum energy spectra. It shows the spectral-weight transfer between regions II and III.

[24] but never experimentally distinguished from the collective plasmon excitations occurring in the same energy loss region.

Region I corresponds to the final states with two holes in the valence band that are not localized to the same atomic site, as indicated by $[4d^{-1}][4d^{-1}]$ and $[4d^{-1}][5sp^{-1}]$ in Fig. 3(a). Here, each set of brackets includes the electron configuration localized to one atomic site. They correspond to the DPE from surfaces, and will not appear in isolated atoms. This type of final states can also be generated from direct DPE from surfaces without involving the core electrons [25]. However, the direct DPE contribution is very small compared with the core-resonant DPE channels in the $M_{4,5}VV$ transition, since the intensities in region I

concentrate only along the $3d$ photoelectron lines, as presented in Fig. 2(a). Thus, the broad peak in region I can be regarded as a shakedown process from the 2-hole state in region II. In contrast to the shakeup processes (**P1** and **P2**) in region III, the DPE pairs *gain* instead of lose energy from the relaxation process of the N-2 electron system by dissociating the 2-hole states bound to specific atomic sites into the delocalized valence bands.

Our observation is consistent with the reported coincidence $N_{2,3}VV$ Auger spectra [19]: The relative intensity in regions I and III are enhanced compared with region II. However, our 2D coincidence spectra firstly demonstrate the spectral-weight transfer of the DPE intensities between regions II and III, while the intensity in region I is unchanged. This important observation is crucial to understand the nature of the enhanced intensities in region III. We experimentally demonstrate that they are due to the single or double interband transitions, which are local excitations in the universal attosecond response to the creation of the core hole [8], before the buildup of the collective plasmon excitations in the extended system [9].

The situation of the $N_{2,3}VV$ Auger transition is more complicated. Since the $4p_{1/2}$ and the $4p_{3/2}$ photoelectrons overlap with each other, we cannot decide the dominating channel solely from the 2D energy distribution in Fig. 2(b). However, the relative intensity of the bandlike region in the E_{sum} spectra of both $N_{2,3}VV$ and $M_{4,5}VV$ Auger transitions are the same. Then we can indirectly conclude that the core-resonant DPE channel also dominates the DPE from Ag in our experiments, while the direct DPE channel can be ignored in the $N_{2,3}VV$ Auger transitions, too.

Autoionization describes the process by which an excited system changes it charge state by the emission of an electron. The Auger effect is a particular example of such a scenario. For autoionization to occur one needs a mixing of two electron configurations, one of which is discrete in energy while the other is continuous. This ensures overlap in energy. The configurations are labeled within an independent particle description. The very existence of electron correlation makes this notation only approximate. This shortcoming is fixed by the introduction of the configuration interaction. In a landmark paper, Fano [26] discusses this and finds that the characteristic time for autoionization to occur is inversely proportional to the configuration interaction strength. Furthermore, the discrete level will develop into a broad feature with a width that scales with the interaction strength. This picture was applied for the explanation of the observed large $4p$ linewidths of the elements ranging from Ag to Xe [5,6]. The one-hole configurations introduced are $4p^{-1}$ and $4d^{-2}4f$. In order to create a $4p^{-1}$ configuration, an energy of 60 eV is required. The continuous configuration is obtained by removing two electrons from the $4d$ band while promoting an electron to a continuum $4f$ level. The energy required to remove two electrons from the $4d$ levels can be read off easily from Fig. 3, and we find a value of 16 ± 3 eV. From a calculation of the unoccupied states, we know that the $4f$ states are 37 ± 10 eV above the Fermi level [27]. This demonstrates that the required energy overlap is ensured.

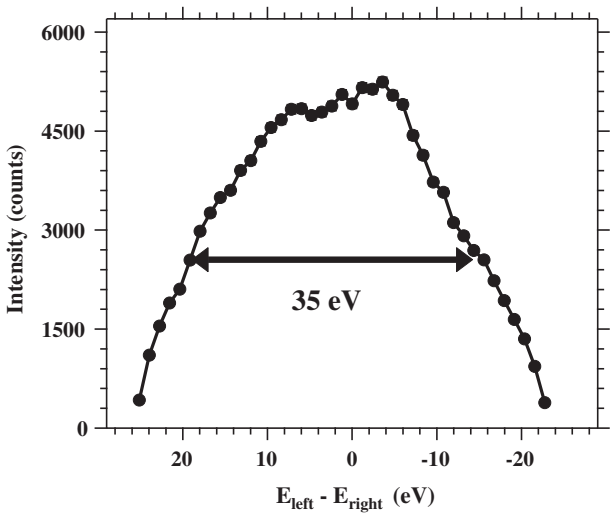

FIG. 4. Energy sharing from the data presented in Fig. 2(b) The energy sum is confined to $E_{\mathrm{sum}}^{\mathrm{max}} - E_{\mathrm{sum}} = 16.4 \pm 2$ eV, which lies within region II.

This results in a strong dynamic fluctuation $4p^{-1} \rightleftharpoons 4d^{-2}4f$ with the consequence of a broad $4p$ photo electron line. Energy conservation fixes the sum energy; hence, the Auger electron line is also broad and escapes identification in standard Auger spectroscopy. This energy relation between the emitted particles can only be observed via coincidence spectroscopy; see Fig. 2(b). It is useful to present the data within region II in a sharing curve. For this we set the energy sum of the electrons to $E_{\mathrm{sum}}^{\mathrm{max}} - E_{\mathrm{sum}} = 16.4 \pm 2$ eV and present the intensity as a function of the energy difference $E_{\mathrm{left}} - E_{\mathrm{right}}$ in Fig. 4. The sharing curve has a width of 35 eV, which is also marked by the arrows of Fig. 2(b). The experiment with other photon energies in the range 96—206 eV revealed a width between 11 and 18 eV. Using the smallest width, we convert this to a time scale of 60 as over which the fluctuations take place. This value is in fair agreement with the theoretical calculation of the time scale to fill an exchange-correlation hole [8].

The fast dynamics is responsible for the continuous energy sharing within the DPE pairs in region II of Fig. 2(b) and results in the shakeup of additional electron hole pairs in the valence band, which contributes to the spectral-weight transfer from region II to III in Fig. 3. This ultrafast electron dynamics cannot be probed by the $M_{4,5}VV$ Auger electrons emitted 2 fs after the photoexcitation, in response to the fully screened $3d^{-1}$ core-hole state.

In conclusion, we have demonstrated that the nature of the core-resonant DPE from a Ag(100) surface depends on the lifetime of the initial core-hole state. The comparison between the sum energy spectra of the $M_{4,5}VV$ and the

$N_{2,3}VV$ transitions demonstrates the spectral-weight transfer from the quasiatomic peak to its low sum energy tail in the $N_{2,3}VV$ transition. It is due to the shakeup processes occurring during the photon excitation process, which creates extra electron-hole pairs. One-step core-resonant DPE is a powerful tool to investigate the ultrafast dynamic screening processes in the very beginning of the photoemission at an attosecond time scale.

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