First Observation on the Photon Energy Dependence of the Partial Auger Transition Rates in Both the $4d_{3/2}$ and $4d_{5/2}$ Auger Decay of Xe

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The relative Auger transition rates are observed to depend significantly on the exciting photon energy. The intensity ratios are found to vary as much as 30% in both the $4d_{3/2}$ and the $4d_{5/2}$ Auger groups when the photon energy is scanned above the $4d$ ionization threshold. The finding emphasizes the need to extend the treatment of the partial Auger transition rates beyond the two-step formulation.

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The Auger effect is usually treated as a two-step process which separates the photoionization and the subsequent nonradiative decay processes. Within the two-step formulation, the number of emitted Auger electrons is proportional to the result of multiplying the Auger component decay rate by the population of the intermediate state. The formulation excludes the possibility that the intensity ratios of Auger transitions originating from the same initial state could vary as a function of exciting photon energy. In more elaborate models, the photoionization and the deexcitation are treated as a single event [1,2]. The emission of the Auger electron is then considered as a resonance in double photoionization which is treated as a full scattering process,

$$\omega + E_0 \rightarrow E^{2+} + \epsilon_{\text{ph}} + \epsilon_A, \qquad (1)$$

where ω is the photon energy and E_0 and E^{2+} are the total energies of the atom in the ground and final ionic states, respectively.

For photon energies where the kinetic energy of the photoelectron ϵ_{ph} is lower than or equal to the kinetic energy of the Auger electron ϵ_A, both the electrons are subject to postcollision interaction (PCI) [1–3]. This makes the Auger electron line asymmetric in shape and shifts it towards higher kinetic energies. At the ionization threshold, the Auger electron line merges into the corresponding resonant Auger electron lines. For high photon energies, PCI effects are absent, and the Auger electron line remains unaffected; it stays at the nominal kinetic energy and has a Lorentzian shape.

No attention has been paid so far to the behavior of the partial Auger transition rates as a function of photon energy. Such a study is important in order to check whether the photoionization and the decay can be considered to proceed as a two-step or a one-step process. In this Letter, we report an experiment where the photon energy was tuned across the energy region $\epsilon_{\text{ph}} \approx \epsilon_A$ and the intensity ratios of the individual Xe $4d$ Auger electron lines were determined as a function of photon energy.

The first high resolution Xe $4d$ Auger electron spectrum was measured in the early seventies by Werme, Bergmark, and Siegbahn [4] using electron beam excitation. Since then the Xe $4d$ Auger decay has been of continuous experimental and theoretical interest (see, e.g., Ref. [5]). Resonant Auger decay of the Xe $4d^{-1}np$ states has been studied since the first observation by Eberhardt, Kalkoffen, and Kunz [6] in a number of reports [3,5,7–9], showing considerable changes in the spectra compared to the normal Auger electron spectrum. Theoretical descriptions of the resonant Auger transitions that involve the effects due to the coupling of the spectator electron with the core holes created by the Auger decay have been found to agree fairly well with experiment [9].

The photon energy range of our experiment covers the Xe $4d$ giant resonance that has attracted a great deal of interest during the last decade [3,10,11]. From these studies it is clear that the total photoabsorption cross section around 100 eV photon energy is dominated by the $4d \rightarrow \varepsilon f$ photoionization cross section. Because of the enormous $4d$ ionization channel, the coupling with the $5s$ and $5p$ ionization channels feeds the $5s$ and $5p$ partial cross sections. Besides, the interchannel interaction between the single- and double-hole ionization channels results in an enhancement of the $5s$ and $5p$ satellite intensities around the $4d$ threshold. For photon energies above 80 eV, the $4d$ partial cross section starts to fall below the total cross section. The simultaneous excitation or ionization of a $5p$ or $5s$ electron borrows intensity from the main $4d$ ionization channel. At 100 eV photon energy, this double ionization channel accounts for about 25% of the total cross section [10,11]. The detected photon energy dependence of the $4d^{-1}5p^{-1}nl$ photoelectron satellite structures [11] indicates the interaction between the various ionization channels. As will be shown later, the interaction between the main and satellite photoionization channels, reported in [3,10,11], needs to be extended to include the Auger channels (1) as well.

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In this Letter, we present the first systematic study of the synchrotron radiation excited Xe $4d$ Auger electron spectra taken at photon energies from near the $4d$ threshold ($4d_{3/2}$: 69.5 eV, $4d_{5/2}$: 67.5 eV), across the double ionization thresholds, to far above the thresholds. The reason that no observations have been reported so far may be connected to the difficulty of obtaining a sufficient intensity for high resolution Auger electron spectra in this photon energy region. Recent developments in the intensity of incident radiation and in the resolution of electron spectrometers have made the present experiment possible.

The experiment was performed at the Finnish beam line (BL 51) [12] at the MAX I storage ring in Lund, Sweden. The beam line consists of a short period undulator and a modified SX-700 plane grating monochromator [13] with a plane elliptical focusing mirror, giving a reasonable photon flux in the energy range of 60 to 600 eV. The gas phase electron spectrometer is isolated from the ultrahigh vacuum of the monochromator by a differential pumping section [12]. This is equipped with a toroidal refocusing mirror that produces a small spot size of about 1 mm in diameter at the source point of the experimental chamber.

The high resolution electron spectrometer [14] is of the hemispherical type with a mean radius of 144 mm. The analyzer is combined with a four-element retarding or accelerating electron lens that focuses electrons onto the entrance slit of the analyzer. Electrons are retarded or accelerated to a constant pass energy before entering the analyzer. A position sensitive detection system is employed in recording the spectra. An efficient differential pumping of the gas cell allows the use of sample gas pressures in the order of 10^{-3}–10^{-4} mbar in the cell. The spectrometer is mounted with the principal axis of the electron lens in the pseudomagic angle of 54.7° versus the horizontal plane of the main component of the electric field vector, which in combination with the high degree of linear polarization of undulator radiation [15,16] allows direct angular independent measurements of branching ratios. The beam line also has another important characteristic for this study: an almost complete absence of higher orders of exciting radiation, which could affect the detection of the photon energy dependence of the relative line intensities in the studied Auger electron spectra.

The Xe $4d$ Auger electron spectra were measured in the photon energy range of 75–160 eV. In order to obtain the spectra with different electron energy resolution and signal to background ratio for each photon energy, several spectra at various spectrometer pass energies (typically 10, 20, and 50 eV) were taken. In order to compare the spectra taken with different pass energies, all the recorded electron spectra have been corrected for the spectrometer transmission by using experimentally determined correction functions [17].

Transmission corrected Xe $4d$ Auger electron spectra taken at photon energies of 76.9, 96.1, and 126.3 eV, using a pass energy of 10 eV, are shown in Fig. 1. In the uppermost spectrum, the photon energy is below the double excitation threshold. The spectrum displays asymmetric photoelectron and Auger electron line shapes characteristic for PCI [1,3,18]. At 96.1 eV photon energy, the photoelectron satellite structures accompanying the $4d$ photoelectron line appear at low kinetic energies, overlapping strongly with the $4d^{-1} \rightarrow 5s^{-2}$ Auger electron lines. In the spectrum taken with 126.3 eV photons these satellites overlap with the $4d^{-1} \rightarrow 5p^{-2}$ Auger group, and the continuous satellite distribution covers the energy region of 0–35 eV. As the double ionization threshold is exceeded, the low kinetic energy normal Auger electron lines are accompanied by the Auger satellites originating from the decay of the doubly ionized states. Above the $4p$ ionization threshold (around 145 eV), the spectrum is further complicated by the overlapping anomalous spectral distribution of the $4p$ photoelectron intensity. The satellite Auger transitions that result from the Auger cascades give their own contribution in the spectrum. The determination of the intensities of the Auger peaks is a difficult task due to the wide variety of the lines superimposed with the continuous energy distribution.

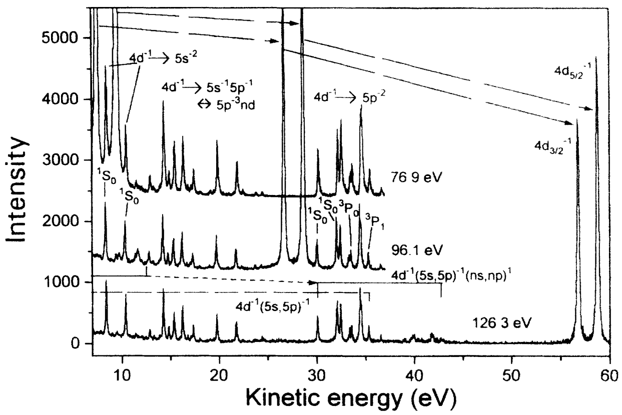

FIG. 1. Experimental Xe electron spectra recorded at photon energies of 76.9 eV (uppermost), 96.1 eV (middle), and 126.3 eV (lowest), and at a pass energy of 10 eV. The spectra display the kinetic energy region of the Auger groups $4d^{-1} \rightarrow 5p^{-2}$, $4d^{-1} \rightarrow 5s^{-1}5p^{-1} \leftrightarrow 5p^{-3}nd$, and $4d^{-1} \rightarrow 5s^{-2}$. The Auger lines for which the branching ratios of Figs. 2 and 3 were determined are indicated in the middle spectrum. The kinetic energy ranges of the $4d$ photoelectron lines and of the discrete (most intense) and continuous $4d$ satellite features are also depicted.

In order to obtain the relative line intensities reliably, the Auger peaks were fitted using the same Voigt line shape and width for all Auger electron lines in a group. Special attention was paid to the appropriate background subtraction and to the accurate separation of the overlapping $4d$ photoelectron and/or satellite lines. In the experiments such an overlap has been minimized by selecting proper photon energies. The determined full width at half maximum (FWHM) of the Voigt profiles of the $4d^{-1} \rightarrow 5p^{-2}$ Auger electron lines were 135, 160, and 220 meV in the spectra taken at pass energies of 10, 20, and 50 eV, respectively.

The intensity ratios of the Auger electron lines, for which the most noticeable effects were observed, are plotted as a function of photon energy in Figs. 2 and 3. For other lines the effects are more difficult to quantify because of the overlapping structures. In Fig. 2 the intensity ratios of the $^3P_1$ and $^1S_0$ lines are shown for the $4d_{3/2}^{-1} \rightarrow 5p^{-2}$ Auger group, and of the $^3P_0$ and $^1S_0$ lines for the $4d_{5/2}^{-1} \rightarrow 5p^{-2}$ Auger group. As can be seen from Fig. 1, these line components are well separated in both groups. Both ratios of Fig. 2 show a clear minimum around 110–120 eV photon energies. $\epsilon_{\rm ph}$ is here around 50 eV, being somewhat larger than ϵ_A [$^1S_0(4d_{5/2})$: 29.95 eV, $^1S_0(4d_{3/2})$: 31.93 eV, $^3P_0(4d_{5/2})$: 33.45 eV, $^3P_1(4d_{3/2})$: 35.20 eV]. As can be seen from the lower spectrum of Fig. 1, the discrete and continuous $4d$ photoelectron satellite features cross the $4d^{-1} \rightarrow 5p^{-2}$ Auger group at the photon energy region where the intensity ratio reaches the minimum.

Figure 3 shows the intensity ratios of the $^1S_0$ lines of the $4d^{-1} \rightarrow 5s^{-2}$ and $4d^{-1} \rightarrow 5p^{-2}$ Auger groups. These ratios now show in turn obvious maxima at slightly lower photon energies around 90–100 eV, corresponding to $\epsilon_{\rm ph}$ of about 30 eV. This indicates that, besides the intensity variations inside both the $4d_{3/2} \rightarrow 5p^{-2}$ and the $4d_{5/2} \rightarrow 5p^{-2}$ Auger groups, there are significant changes also in the line intensities belonging to the $4d^{-1} \rightarrow 5s^{-2}$ and $4d^{-1} \rightarrow 5p^{-2}$ Auger groups. Worth noticing is also (see Fig. 1) that the $4d^{-1} \rightarrow 5s^{-2}$ Auger transitions (at 8.30/10.27 eV) coalesce in energy with the $4d$ photoelectron satellite transitions at the photon energy region where the intensity ratios in Fig. 3 have their maxima.

The discovered photon energy dependence of the intensity ratios of the Auger electron lines is a surprisingly large effect, although it has been so far completely disregarded as far as we know. Earlier it has been observed that the intensity ratios of parent lines differ completely in the resonant and normal Auger electron spectra. The difference arises from the changes in the mixing of core-hole states induced by the spectator-core coupling [9]. For the first time it is now observed experimentally that there are large variations in the intensity distribution of Auger electrons even at energies well above the threshold. The intensity ratios of the Auger electron lines are most dramatically enhanced in the photon energy range where the kinetic energies of the electrons associated with the $4d$ photoelectron satellite transitions equal to ϵ_A. The fact that the change in the partial transition rates is smooth excludes the possibility that the intensity variation is caused by an unresolved overlap of the Auger electron and photoelectron satellite lines. Thus there exists a real effect, discovered with the aid of present high resolution experiment and careful data handling, within the error limits indicated in Figs. 2 and 3. At the moment we cannot, however, say how far above threshold the partial transition rates become constant. The degree of linear polarization, even if not complete, and the angular dependence, even if weakly present, could not cause variations as large as 30% observed by experiment.

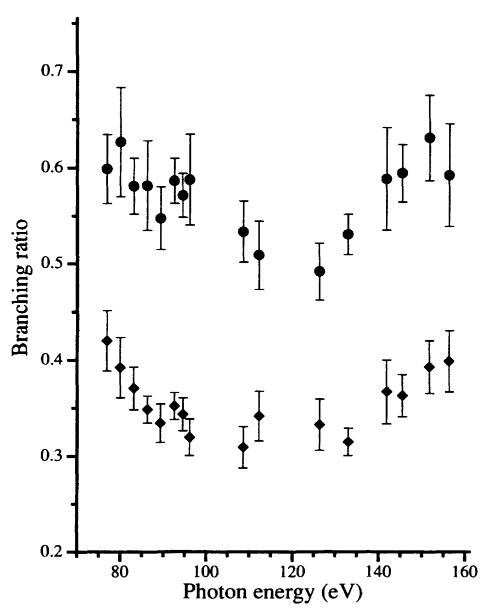

FIG. 2. The circles in the upper part show the intensity ratio of the $4d_{5/2}^{-1} \rightarrow 5p^{-2}(^3P_0)$ and $4d_{5/2}^{-1} \rightarrow 5p^{-2}(^1S_0)$ Auger electron lines, and the diamonds in the lower part show the intensity ratio of the $4d_{3/2}^{-1} \rightarrow 5p^{-2}(^3P_1)$ and $4d_{3/2} \rightarrow 5p^{-2}(^1S_0)$ Auger electron lines. The error bars are mainly due to uncertainties in curve fitting and background subtraction (and based on scattering of results from several fits).

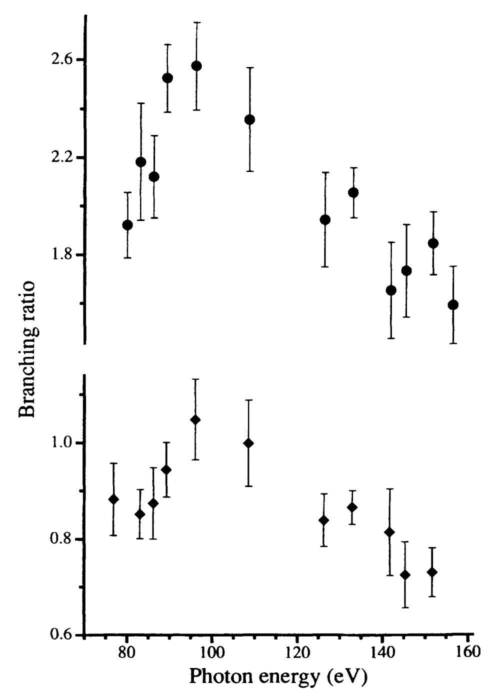

FIG. 3. The circles in the upper part show the intensity ratio of the $^1S_0$ lines in the $4d_{5/2}^{-1} \rightarrow 5s^{-2}$ and $4d_{5/2}^{-1} \rightarrow 5p^{-2}$ Auger groups, and the diamonds in the lower part show the same ratio in the $4d_{3/2}$ Auger group. See caption of Fig. 2 for error bars.

The present observation shows that there is an urgent need for a better theoretical understanding of the core ionization processes. The observed photon energy dependence in the intensity distribution of both the $4d_{3/2}$ and $4d_{5/2}$ Auger transitions, not allowed within the two-step formulation, emphasizes the need to treat reactions (1) properly. The present experimental finding clearly presses the need to extend the theoretical treatment of the partial Auger transition rates beyond the two-step model.

The coupling between the main 5s and satellite photoionization channels has earlier been realized to play an important role in the redistribution of the oscillator strengths [19]. It seems obvious that the interaction needs to be extended to include the Auger channels as well. The treatment of the Auger process as a one-step transition from the neutral initial state to the final state with two outgoing electrons [Eq. (1)] results in double ionization (e.g., $5p^{-2}\varepsilon_A d\varepsilon_{\rm ph} f$) channels. These are comparable with the channels where the 4d photoionization is accompanied by the simultaneous excitation or removal of an outer shell electron [e.g., $4d^{-1}5p^{-1}(n,\varepsilon)p\varepsilon_{\rm ph} f$], or with the channels [e.g., $5p^{-2}(n,\varepsilon)d\varepsilon_{\rm ph} p$] which result from the interaction between the 5s hole and $5p^{-2}(n,\varepsilon)d$ excited states, or with the channels [e.g., $4d^{-2}(n,\varepsilon)f\varepsilon_{\rm ph} d$] which originate from the mixing of the $4p^{-1}$ and $4d^{-2}(n,\varepsilon)f$ states. So far there has been no attempt to study the interaction between all these and the single photoionization channels. Theory has to face not only the complexity arising from the inclusion of a large number of channels, but also the question how to proceed with a system which consists of an ion and two or more electrons in the continuum. Electron correlation seems to play a prominent role in the present study, most probably also because the kinetic energies of electrons involved are low; the studied Auger spectrum appears at 0–37 eV.

In conclusion, the intensity distribution of the Xe 4d Auger transitions has been studied at the photon energy region $\epsilon_{\rm ph} \approx \epsilon_A$. A remarkably strong photon energy dependence in the intensity ratios of the Auger electron lines has been found also far above the threshold. The relative intensities are observed to vary as much as 30% when scanning the photon energy from the ionization threshold to 160 eV photon energy. The changes seem to correlate with the creation of the $4d^{-1}(5s,5p)^{-1}(n,\varepsilon)l\varepsilon_{\rm ph} l$ channels.

This is the first observation of the influence of the photon energy on the partial Auger transition rates. The finding clearly indicates that the two-step formulation of the Auger process becomes violated in a broad photon energy region. From the present work it is clear that the Auger process has to be definitely described as a one-step process. The interaction between various single and double ionization channels needs to be investigated as well.

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