Electronic-state lifetime interference in the resonant Auger decay of krypton

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Resonant Auger electron spectra from the close lying $3d_{3/2}^{-1}5p$ and $3d_{5/2}^{-1}6p$ core-excited states of Kr have been measured. The intensities of the transitions to the $4p^{-2}5p$ and $4p^{-2}6p$ final states have been followed as a function of the exciting photon energy. The effects caused by the lifetime interference between the two Auger decay channels are interpreted by using the one-step picture of the excitation-deexcitation process, with the help of *ab initio* calculations of the electron wave functions and transition matrix elements. Some aspects beyond the spectator model used are discussed. [S1050-2947(97)06808-X]

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I. INTRODUCTION

Interference effects can play an important role in various atomic inner-shell processes whenever several transition channels have comparable probabilities, for example, in the case of the Auger decay of core-to-Rydberg resonances. A well-studied example is the lifetime-vibrational interference in the Auger decay of the core-hole states of molecules [1–4]. Auger-electron intensities and line profiles can also be affected by the interference between the Auger decay and direct photoionization channels [5]. The lifetime interference has recently been studied in the radiative decay of the core-excited states, split by the lowered symmetry in solids [6] and molecules [7]. The effect has been found to be prominent in the Ar KLL spectator Auger decay [8]. The inteference between numerous bound and also continuum states is very strong in this case due to the broadness of the K-shell excitations. On the other hand, the interaction between the core-excited states can be neglected in the Mg $2p$ excitations, where the width of the states is sufficiently small [9].

In the present study, we consider the lifetime interference effects in the resonant Auger decay from two adjacent atomic core-excited electronic states. The experimental data derive from the Kr $3d_{3/2}^{-1}5p \rightarrow 4p^{-2}n'p$ and $3d_{5/2}^{-1}6p \rightarrow 4p^{-2}n'p$ resonant Auger-electron spectra, selectively excited by synchrotron radiation. An important feature of this selection of core-excited states is that they do not belong to the same Rydberg series, since different $3d$ spin-orbit split components are excited. By chance, these states are energetically close to each other (separated by about 1.7 times their lifetime width), at the same time being well separated from the other Rydberg excitations. This simplifies considerably the interpretation of the experimental results with the help of the calculations of atomic orbitals and transition matrix elements.

II. EXPERIMENT

The electron spectra of krypton were measured at the soft x-ray undulator beamline 51 (the Finnish beamline) [10] at the MAX synchrotron radiation laboratory. A modified SX-700 plane grating monochromator [11] was operated at the photon energy resolution of about 16 meV. The Auger-electron spectra (presented in Fig. 1) have been recorded at the magic angle relative to the electric vector of the photon beam using an SES-200 hemispherical electron spectrometer [12] that provides an electron energy resolution of about 30 meV at 20-eV pass energy. The pass energy of 40 eV was used when recording the constant final-state spectra (Figs. 2 and 3).

III. THEORETICAL BASIS

Cesar and Ågren have demonstrated [13] that the lifetime interference in the radiative or nonradiative decay of nearby

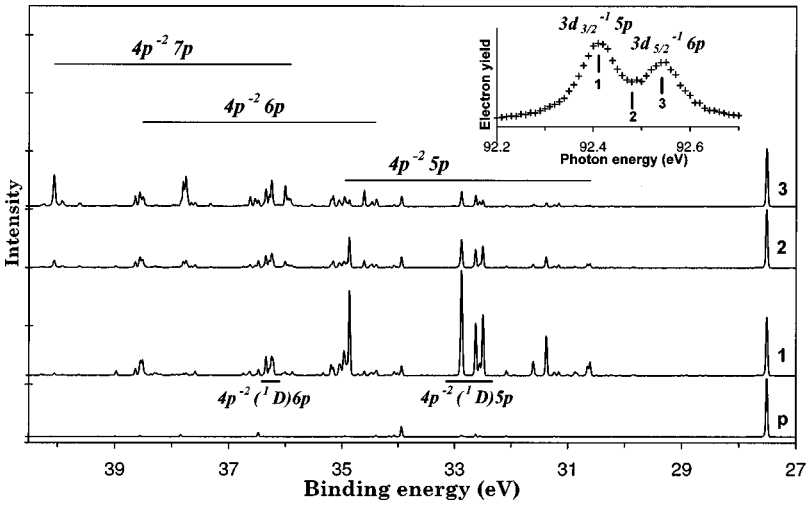

FIG. 1. Resonant Auger spectra of Kr, excited at different photon energies that are marked (1–3) in the inset (total electron yield spectrum). Photoelectron spectrum (p) is recorded at $\hbar\omega = 90.0$ eV. Binding-energy ranges for the constant final-state spectra of Fig. 2 are marked by horizontal bars under (1).

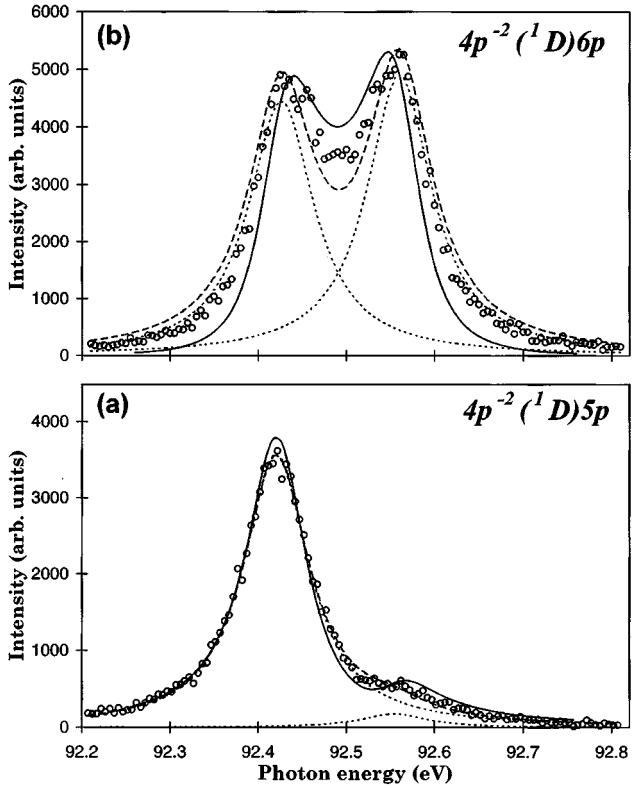

FIG. 2. Constant final-state spectra of the $4p^{-2}(^1D)5p$ (a) and $4p^{-2}(^1D)6p$ (b) groups, over the photon energy range of the $3d_{3/2}^{-1}5p$ and $3d_{5/2}^{-1}6p$ excitations. Dashed lines: fit by two Lorentzian curves, solid lines: fit including interchannel interference.

vibronic as well as electronic states can be treated quite analogously. The interference effects appear naturally in the one-step resonant scattering model of the photoexcitation and Auger processes [14,15], where the latter is mediated by intermediate resonant core-excited states. In this model, the cross section for absorbing a photon $\hbar\omega$ and emitting an (Auger) electron is

$$\sigma(\hbar\omega)=\int_0^\infty \frac{d\sigma}{d\epsilon_A}d\epsilon_A \propto \sum_f \left|\langle f|D|0\rangle+\sum_i \frac{\langle f|Q|i\rangle\langle i|D|0\rangle}{\hbar\omega-(E_i-E_0)+i\Gamma_i/2}\right|^2, \tag{1}$$

where the summations are over the intermediate states $|i\rangle$ and the Auger final states $|f\rangle$. The atomic ground state $|0\rangle$ is excited by the dipole interaction D to the intermediate state, which decays to the final state due to the Coulomb interaction Q. E_0, E_i, and ϵ_A stand for the ground state, intermediate state and Auger-electron energy, respectively, and Γ_i are the lifetime widths of the core-hole intermediate states. The direct term $\langle f|D|0\rangle$ gives the photoionization directly to the state $|f\rangle$ and is usually small compared to the resonant processes at the near-threshold excitations. Due to the energy conservation,

$$\epsilon_A=\hbar\omega-(E_f-E_0), \tag{2}$$

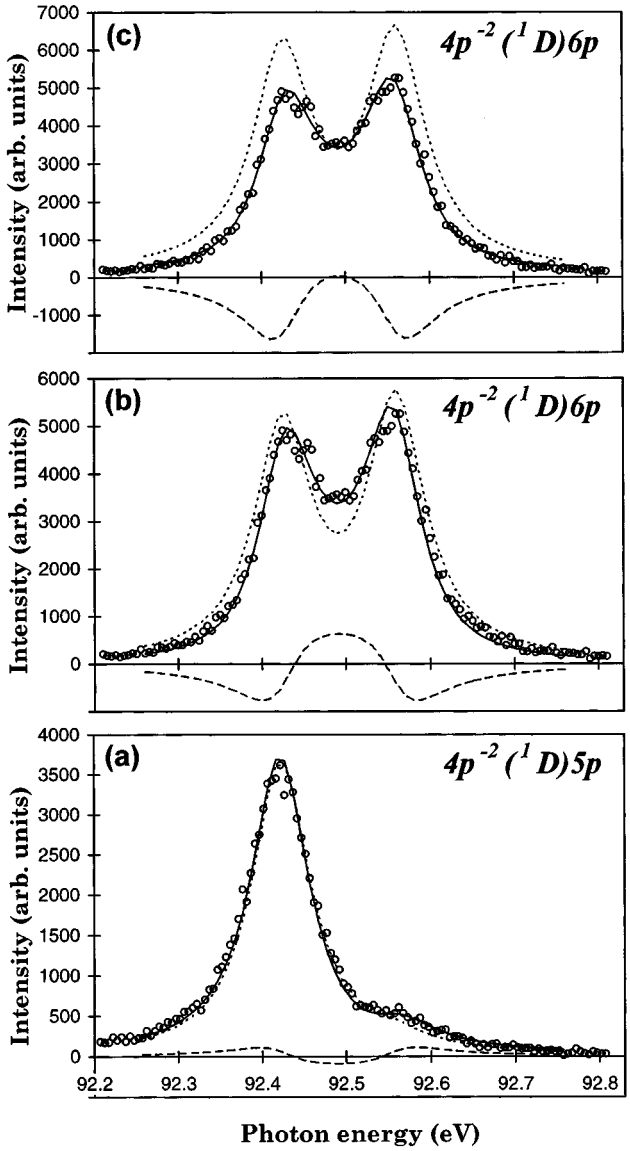

FIG. 3. Constant final-state spectra of the $4p^{-2}(^1D)5p$ (a) and $4p^{-2}(^1D)6p$ (b,c) groups, fitted (solid lines) using the reduced interference [(a) and (b)] and three-channel interference (c). Dotted lines: independent, dashed lines: interference contributions.

where E_f is the energy of the final state.

When the transitions to a single final state are followed as a function of photon energy and the direct photoionization is not taken into account, Eq. (1) gives a superposition of Lorentzians (hereinafter referred to as independent terms) peaking at the resonance energies $\hbar\omega_i=E_i-E_f$, and phase-dependent interchannel interference terms. The latter become important, if the independent terms overlap considerably. Only the channels leading to the same final state can interfere and the summation over the final states adds no interference terms.

IV. RESULTS AND DISCUSSION

A. General features

Tunable synchrotron radiation has been used to create the Kr $3d_{3/2}^{-1}5p$ ($\hbar\omega$=92.425 eV) and $3d_{5/2}^{-1}6p$ ($\hbar\omega$=92.560 eV) core-excited initial states of the Auger decay. The life-

time width of these states (about 81 meV [16]) is somewhat smaller than their energy separation of 135 meV, so that the states overlap strongly, but are still separable from each other. The closest neighboring core-excited states $3d_{5/2}^{-1}5p$ and $3d_{5/2}^{-1}7p$ lie about 1.2 eV below and 0.5 eV above these states [16], respectively, which strongly suppresses their contributions in the photon energy range in question. The $3d_{3/2}^{-1}5p$ and $3d_{5/2}^{-1}6p$ states can decay to the same $4p^{-2}n'p$, $n'=5,6,7,\ldots$ states by the spectator and shake resonant Auger transitions [17], being therefore suitable for studying the lifetime interference effects.

B. Auger-electron spectra

Figure 1 presents the Auger electron spectra recorded at three different photon energies indicated by 1–3 in the inset. A spectrum taken at the off-resonance energy of 90.0 eV is also shown (p). The binding-energy ranges of the $4p^{-2}n'p$ final states are indicated in the figure. The transitions to the $4p^{-2}5p$ states dominate the $3d_{3/2}^{-1}5p$ decay spectrum, but rather strong shake-up processes also populate the $4p^{-2}6p$ states. The $4p^{-2}7p$ states are reached by very strong $6p\rightarrow 7p$ shake-up transitions in the $3d_{5/2}^{-1}6p$ spectrum, where the spectator transitions to the $4p^{-2}6p$ states are somewhat less intense and the $6p\rightarrow 5p$ shake-down transitions to the $4p^{-2}5p$ states are rather weak. The spectrum recorded between the two resonances has a mixed character of these two spectra, and would just be their superposition, if there were no interference effects. These effects can, however, strongly alter the absolute intensities and branching ratios of the Auger electron lines.

C. Constant final-state spectra

We selected two groups of lines, $4p^{-2}(^1D)n'p, n'=5,6$ (marked in Fig. 1), and followed their intensities as a function of photon energy. Figure 2 displays the photon energy dependence of the total intensity of the $4p^{-2}(^1D)5p$ and $4p^{-2}(^1D)6p$ line groups [spectra (a) and (b), respectively], normalized to the constant photon flux. The dashed lines represent fits to the experimental data of two Lorentzian curves (dotted lines, with 81-meV full width at half maximum) peaking at the resonance energies. These curves correspond to an approximation of Eq. (1), where only the independent terms are included. The cross section (1) should be convoluted with the distribution of the exciting photons in order to describe the experiment better [18,19], but the effect is negligible due to the narrowness of the photon band used. Spectrum (a) is dominated by the decay from only one resonance and the fit describes the data rather well. Much larger discrepancies can be seen in the case of the $4p^{-2}(^1D)6p$ group (b), indicating a strong interference.

D. Interference between two resonant decay channels

Before including the interference terms some approximate calculations were carried out in order to predict the phase factors of these terms. The dipole and Coulomb matrix elements of Eq. (1), involving coupled many-electron wave functions, can be separated into the radial parts constructed from one-electron orbitals and the geometrical factors C^d and C^q. In the pure LS-coupling approximation, these factors are independent of the spin-orbit splitting of the $3d$ core-hole states. One can now express the dipole transition matrix elements simply as $C^d\langle 5p|r|3d\rangle$ and $C^d\langle 6p|r|3d\rangle$. The Auger transition matrix elements contain in this approximation a common term $C^q\langle 4p4p|\,\frac{1}{r}\,|3d\epsilon l_A\rangle$, which describes the $3d^{-1}\rightarrow 4p^{-2}\epsilon l_A$ Auger decay. The matrix elements of the spectator and shake transitions then differ only by the overlap integrals $\langle n'p|np\rangle$ between the excited electron's orbital in the Auger initial and final states (the shake model). In the lifetime-vibrational interference in molecules, similar overlap integrals represent the Franck-Condon factors of the nuclear wave functions. At this stage we also neglect the direct terms, which are very weak as seen from the spectrum (p) of Fig. 1. For the $4p^{-2}(^1D)6p$ final states, for example, Eq. (1) then reads

$$\sigma(\hbar\omega)\propto\left(C^dC^q\left\langle 4p4p\left|\frac{1}{r}\right|3d\epsilon l_A\right\rangle\right)^2\times\left|\frac{\langle 6p|5p\rangle\langle 5p|r|3d\rangle}{\hbar\omega-\hbar\omega_{3d_{3/2}^{-1}5p}+i\Gamma/2}+\frac{\langle 6p|6p\rangle\langle 6p|r|3d\rangle}{\hbar\omega-\hbar\omega_{3d_{5/2}^{-1}6p}+i\Gamma/2}\right|^2, \tag{3}$$

where the same width Γ has been used for both core-excited states. The common factors $C^q\langle 4p4p|\,\frac{1}{r}\,|3d\epsilon l_A\rangle$ and C^d affect only the absolute intensities; they do not determine the interference pattern. The remaining matrix elements have been calculated using the code of Cowan [20] and are given in Table I.

TABLE I. Calculated dipole radial matrix elements and overlap integrals (in atomic units) of the excited electron's wave functions in the Auger initial and final states.

	Dipole radial matrix elements	
	$\langle 5p\|r\|3d\rangle$	$\langle 6p\|r\|3d\rangle$
	0.031	0.017
	Overlap integrals	
n'	$\langle n'p\|5p\rangle$	$\langle n'p\|6p\rangle$
5	0.90	0.27
6	−0.43	0.63
7	−0.04	−0.73

The calculated shake probabilities (as the squares of the overlap integrals) agree well with the experiment and previous calculations [21]. We are, however, mostly interested in the signs of the matrix elements that determine whether the interference is constructive or destructive at a certain photon energy. The solid curves in Fig. 2 take the interference into account, with the phase factors obtained using the values of Table I. The $\langle 6p|5p\rangle$ and $\langle 6p|6p\rangle$ overlap integrals have opposite signs, which leads (with the given separation and widths of the excited states) to constructive interference in the photon energy range between the two resonances. This can be seen as intensity enhancement in spectrum (b) of Fig. 2. The interference becomes destructive at photon energies below the $3d_{3/2}^{-1}5p$ and above the $3d_{5/2}^{-1}6p$ resonances. In

contrast, the overlap integrals involved in the transitions to the $4p^{-2}5p$ and $4p^{-2}7p$ final states have the same signs and the interference in the region between the resonances is destructive, as seen in spectrum (a). The results for the $4p^{-2}7p$ group are not presented, because in this case one resonant channel, the $5p\rightarrow 7p$ shake-up process, is very weak and the interference between the two channels hardly observable. Similar interference effects have recently been observed in the resonant Auger decay of the $1s^{-1}np, n=3,4$ states of Ne [22].

E. Influence of final states

Although the regions of constructive and destructive interference are in qualitative agreement with the experiment, the effect is clearly overestimated in Fig. 2. This may be at least partly due to the fact that there are a number of $4p^{-2}(^1D)6p(^{2S+1}L_J)$ final states in the Auger decay spectrum and Fig. 2 gives the total intensities of the transitions to these states. The interference effect is the strongest, if both intermediate resonance states give equal contributions to the total transition amplitude to each final state (see, e.g., Ref. [13]). The contributions seem indeed to be well balanced in spectrum (b). This is, however, an average over all included strongly overlapping final states. For each single final state, the balance may be rather different, with one channel dominating. This obviously reduces the strength of the interference, which can be taken into account by adding a scaling factor k $(k=0-1)$ to the interference term. The curves in spectra (a) and (b) of Fig. 3 represent such a ''reduced interference'' effect. The best fit was achieved with $k=0.5$ in both cases. There are some single lines inside these groups that display stronger interference effects than the group in average. These features are beyond the scope of our theoretical approach, since they need the coupling of the excited electron to the core to be taken into account properly, which is not done in the used spectator model.

F. Contributions from other channels

So far we have ignored the direct transitions which can be seen to weakly populate the Auger final states in the photoelectron spectrum (p) of Fig. 1. The intensity of these structures is only in the order of 1% of the resonant structures, corresponding to roughly ten times smaller transition amplitudes. However, by adding such a weak nonresonant channel to the two resonant channels in Eq. (3) one can, with a suitable choice of sign, arrive at a very good agreement with the experiment, as shown for spectrum (c) in Fig. 3. Note that somewhat larger resonant matrix elements are needed in this case. The ''reduced interference'' (b) as well as the three-channel interference (c) seem to be equally well suited to describe the measured spectra and it is therefore not possible to determine their partial contributions. Most probably both mechanisms play some role.

The interaction with the other neighboring resonant channels should also be considered. An estimate based on the line intensities, widths and excitation energies in the absorption spectrum [16] together with the calculated shake overlap integrals shows that the largest contribution comes from the $3d_{5/2}^{-1}5p$ decay channel via the $5p\rightarrow 6p$ shake-up transitions, which is still less than 5% of the ampitudes of the $3d_{3/2}^{-1}5p$ and $3d_{5/2}^{-1}6p$ channels at their resonance energies. We thus expect the other resonant channels to influence the spectra less than the direct channel, especially in the region between the $3d_{3/2}^{-1}5p$ and $3d_{5/2}^{-1}6p$ excitations. For more accurate calculations they can be taken into account by simply expanding Eq. (3).

V. CONCLUSIONS

In conclusion, when the same Auger final states are populated from two (or more) close-lying core-hole states, strong interference effects influence the Auger electron line intensities. The interference contributions can be strong even in the spectra recorded exactly at the resonances. A straightforward comparison between the experimental line intensities and calculations based on the two-step model is not feasible in such cases. The interference pattern depends crucially on the characteristics of the transitions populating the final states under consideration. Rather simple *ab initio* calculations seem to predict qualitatively this dependency, which is connected to the signs of the matrix elements, which in turn depend on the shapes of the radial wave functions of the excited electron in the core-excited intermediate and final states. The observed reduced interference effect can be understood by going beyond the used spectator model, but also by taking into account the nonresonant photoionization.

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