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Autoionization of the Ca $2p^5 3d$ core resonances: Breakdown of the spectator model

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The decay of the photon-excited $2p^5 3s^2 3p^6 3d4s^2$ core resonances of atomic Ca has been studied by electron spectroscopy and by multiconfiguration calculations of the autoionization rates. Strong correlation effects give rise to complicated line structures that are mostly due to the autoionization of the resonances into the $3p^4 3d4s^2 \epsilon l$, $3p^4 3d4p^2 \epsilon l$, and $3p^4 3d^3 \epsilon l$ continua. The breakdown of the spectator model, which is caused by the collapse of the $3d$ orbital, manifests itself in the dramatic differences between the spectra excited via the two resonances split by the spin-orbit and $2p$-$3d$ interactions.

Atomic Ca has turned out to be one of the key elements for the study of many-electron dynamics in atoms. Upon inner-shell excitation the low-lying empty $3d$ orbital can collapse into a corelike orbital with an energy close to that of the $4s$ orbital. The near degeneracy of the $3d$ and $4s$ energies in Ca I and Ca II in the presence of a core hole gives rise to strong configuration interactions, which manifest themselves in complicated absorption spectra and a manifold of satellites in the photoelectron spectra. Characteristic for the $3p$ excitations is the dependence of the $3d$-orbital collapse on the configuration, the degree of ionization, and even the angular momentum coupling of the electronic state. The difference between $3d$ orbitals in the ^1P and ^3P states of the $3s^2 3p^5 3d$ configuration in Ca III (Ref. 1) is a case in point. In a series of experimental (see Refs. 2–5 and references therein) and theoretical (see Refs. 6–10 and references therein) investigations the Ca $4s$ and $3p$ excitations have been studied in some detail. The $3p$ excitations are difficult to unravel due to the strong $3p$-$3d$ interaction coupled with the abovementioned sensitivity of the $3d$ orbital to its environment. Transitions of $2p$ electrons into collapsed $3d$ orbitals are expected to dominate the $2p$ excitation spectra and should be easier to unravel since the $2p$-$3d$ interaction is much weaker than the $3p$-$3d$ interaction. This is borne out by absorption[11] and ion-yield spectra[12] which display two strong resonances ascribed to excitations to the spin-orbit-split $2p^5(^2P_{1/2}, ^2P_{3/2})3s^2 3p^6 3d4s^2$ final states. Calculations of the $2p^6 \rightarrow 2p^5 nd,ns$ transitions in Ar-like ions support this assignment.[13] A very elaborate experimental and theoretical study[14] of the L Auger spectra excited by electron bombardment demonstrates that the anomalous intensity distributions are caused by strong correlation effects in the ionic $2p$-hole state due to the partial collapse of the $3d$ orbital. In order to gain more insight in these correlation effects and to test the validity of the spectator model frequently used in the analysis of the decay of rare-gas core resonances,[15,16] we studied the decay of the photoexcited $2p^5 3s^2 3p^6 3d4s^2$ resonances, both experimentally and theoretically. The content of the spectator model is briefly that the excited electron should have no effect on the decay of the inner-shell hole. Thus, the Auger spectrum following the decay of any $2p^5 3d$ state should look like the decay of $2p^5$ except for an energy displacement due to screening.

The experimental investigations were performed at the FLIPPER I wiggler-undulator beamline at the Hamburger Synchrotronstrahlungslabor (HASYLAB).[17] The Ca vapor beam was produced by an oven indirectly heated by electron bombardment[18] and collimated by a separately heated nozzle. The Ca beam crossed the monochromatized synchrotron radiation in the source volume of a cylindrical mirror analyzer (CMA) which was used to determine the energy of the electrons emitted close to the magic angle 54°44′ with respect to the polarization vector of the light. In order to improve the energy resolution the fast autoionization electrons ($E_{\text{kin}} > 230$ eV) were retarded by a constant electric field ($eU_{\text{ret}} = 200$ eV) before they entered the CMA. The energy resolution thus achieved is given by $\Delta E_{\text{kin}} = 0.01(E_{\text{kin}} - eU_{\text{ret}})$. At the Ca $2p$ threshold the bandwidth of the monochromatized photon beam was $\Delta\hbar\omega \geq 1$ eV.

The calculations were carried out using the suite of programs written by Cowan.[19] The calculations are based on rather large basis sets using the relativistic Hartree-Fock (HF) approach described by Cowan and Griffin[20] to construct the basis. In order to take the variability of, in particular, the $3d$ orbital into account, overlap factors were included in the calculations of R^k and dipole integrals.

The $4s$, $3p$, and $3s$ photoelectron lines and the satellite lines observed in a spectrum taken at $\hbar\omega = 310$ eV, i.e., far *below* the $2p$ thresholds, are shown in the right-hand part of Fig. 1. In addition to these lines, a host of new lines emerge in the range of kinetic energies below 50 eV when the photon energy is chosen *above* the $2p$ thresholds. A spectrum recorded at $\hbar\omega = 406$ eV is presented in the left-hand part of Fig. 1. The Ca^+ $3p^5 4s^2 \rightarrow Ca^{2+}$ $3p^6$ Auger decay and the second step Ca^{2+} $3p^4 4s^2 \rightarrow Ca^{3+}$ $3p^5$ Auger decay gives rise to the very sharp lines in the low-energy part. The width of these lines ($\Delta E_{\text{kin}} = 0.15$

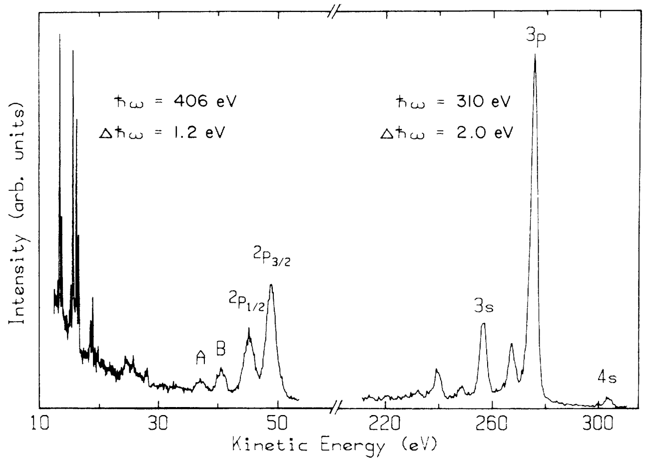

FIG. 1. Photoelectron spectra of atomic Ca. Left-hand side: $\hbar\omega=406$ eV; $\Delta\hbar\omega=1.2$ eV; $\Delta E_{\text{kin}}=0.01E_{\text{kin}}$. Right-hand side: $\hbar\omega=310$ eV; $\Delta\hbar\omega=2$ eV; $\Delta E_{\text{kin}}=0.01E_{\text{kin}}$. Both spectra are corrected for the analyzer transmission but displayed on different intensity scales.

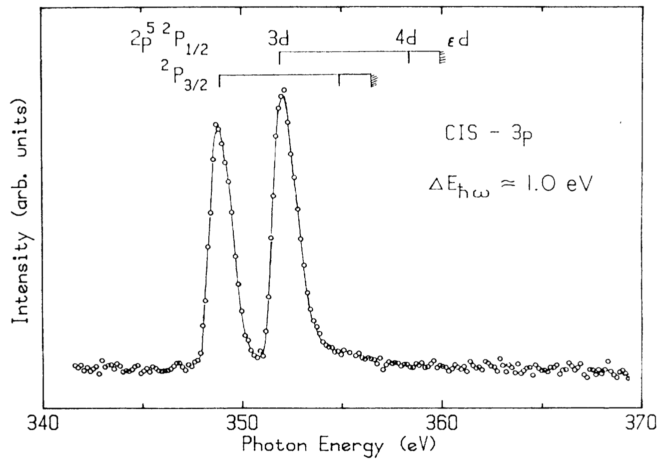

FIG. 2. Relative partial $3p$ cross section given by the constant-ionic-state (CIS) spectrum of the Ca $3p^54s^2$ photoline in the region of the $2p$-$3d$ resonances and $2p$ thresholds; $\Delta\hbar\omega=1.0$ eV.

eV, the natural linewidths are considerably smaller) reflects the resolving power of the electron-energy analyzer, while the width of the $2p_{1/2,3/2}$ photoelectron lines and of the two satellite lines (indicated by A and B) is determined by the bandwidth $\Delta\hbar\omega=1.2$ eV of the photon beam. Due to the rather limited resolution the splitting of the $2p_{1/2,3/2}$ photoelectron lines and their satellites predicted by Weber *et al.*[14] on the basis of their analysis of the L_{23} Auger spectra, could not be detected. According to their calculations ionic state configuration interaction gives rise to two $2p^5$ $J=\frac{1}{2}$ and six $2p^5$ $J=\frac{3}{2}$ states with appreciable $2p^54s^2$ components. Our calculations place the $2p^53d^2$ satellites about 0.8 eV below the $2p^54s^2$ thresholds. Based on these calculations we assign the two satellites at $E_{\text{kin}}=37.1$ eV (satellite A) and $E_{\text{kin}}=40.7$ eV (satellite B) to the spin-orbit-split $2p^5_{1/2,3/2}4p^2$ final states in analogy with the strong $4p$ satellites observed in $4s$ ionization.[21] The $2p$ binding energies (for $2p_{3/2}$, $E_B=357.0 \pm 0.5$ eV; for $2p_{1/2}$, $E_B=360.6\pm0.5$ eV) are consistent with those determined from Auger[14] and absorption[11] spectra.

Turning now to the region *close to* the $2p$ threshold, we show in Fig. 2 the relative cross section of the $3p$ photoelectron line, which resembles the corresponding absorption[11] and ion yield[12] spectra. The two strong resonances, centered at $\hbar\omega=348.8\pm0.5$ eV and at $\hbar\omega=352.0\pm0.5$ eV are ascribed to excitations to $2p^5(^2P_{1/2,3/2})3s^23p^6$-$3d4s^2$ states. The $3p$ partial cross section does not show any marked enhancement at the photon energies of the $2p\rightarrow4d$ absorption lines.[11] From the width of the resonances, taking the bandpass of the monochromator into account, a value of less than 0.5 eV has been determined for the width of the $2p^53s^23p^63d4s^2$ levels. This value is consistent with a calculated width of less than 0.5 eV. The energy splitting of the two resonances is markedly lower than the distance between the $2p_{1/2}$ and $2p_{3/2}$ ionization energies. From the area of the resonances a $^2P_{3/2}$:$^2P_{1/2}$ intensity ratio of 1:1.2 has been determined. This ratio is smaller than the ratio of 1:1 obtained for the oscillator strength of the $2p\rightarrow3d$ excitations by summing up the strength of all decay channels of both resonances, i.e., the total electron intensity with $E_{\text{kin}}>170$ eV in the photoelectron spectra. However, both ratios deviate markedly from the statistical ratio of 2:1 that is consistent with the observed ratio between the $2p_{3/2}$ and $2p_{1/2}$ photoelectron lines displayed in Fig. 1. These findings can be explained by describing the resonances in intermediate coupling. The collapse of the $3d$ orbital in the $2p^53d$ excited state gives rise to a $2p$-$3d$ interaction comparable to the $2p$ spin-orbit splitting. The calculations ascribe appreciable transition probability to the

$$\text{Ca } 2p^63s^23p^64s^2(^1S_0)\rightarrow \text{Ca* } 2p^53s^23p^63d4s^2(^3D,{}^1P)$$

excitations (the excitation to ^3P is much weaker) and give an intensity ratio ^3D:^1P of 1:1.6. The $2p$-$3d$ exchange interaction can however be expected to be overestimated in a HF calculation for the mean energy[1] and if this interaction is reduced by 25% a ratio close to 1:1 is obtained. This calculation also distributes the intensity over more than one state for each resonance.

Consider now the electron spectra taken *at* the $2p$-$3d$ resonance energies ($\hbar\omega=348.8$ eV and $\hbar\omega=352.0$ eV). These show [Fig. 3(a)] besides the $3s$ photoelectron line enhanced by $2p^53s^23p^63d4s^2\rightarrow 2p^63s3p^64s^2\epsilon l$ autoionization, a prominent group of lines in the range $55\leq E_B\leq 75$ eV. The most striking feature of these lines is the dramatic change in structure when the photon energy is tuned from the low-energy resonance to the high-energy resonance. Strength and energy make the Ca $2p^53s^23p^63d4s^2\rightarrow 2p^63s^23p^43d4s^2\epsilon l$ autoionization the most likely origin of these lines. However, considering the $3d$ electron as a spectator would suggest a structure similar to that following the decay of the $2p$ hole,[14] as already mentioned, and cannot be reconciled with either the form or the large change in intensity distribution of the spectrum between the two resonances. In order to gain insight

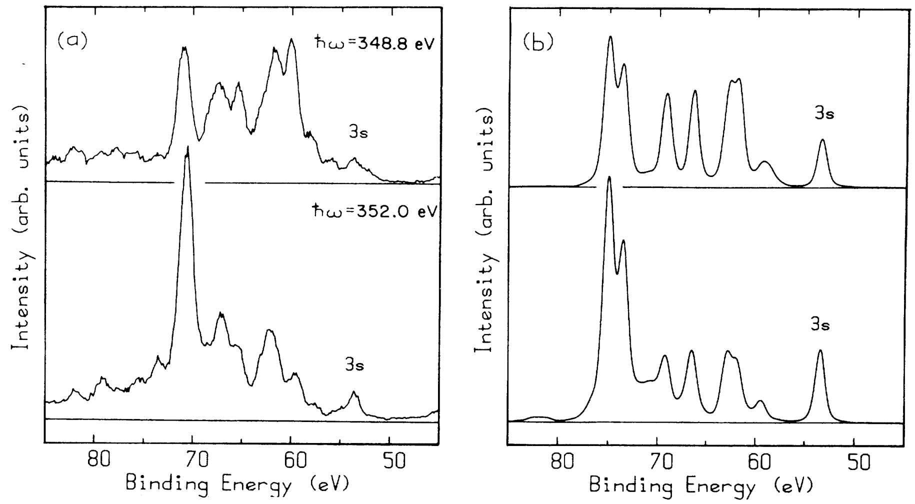

FIG. 3. (a) Photoelectron spectra of atomic Ca taken at the $2p$-$3d$ resonance energies; $\Delta E_{\mathrm{kin}} = 0.01(E_{\mathrm{kin}} - 200\ \mathrm{eV})$, $E_{\mathrm{kin}} = \hbar\omega - E_B$. The relative intensities of the spectra have been obtained by adjusting the intensity ratio of the $3p$ photoelectron lines [not included in Fig. 3(a)] to the ratio of the experimental $3p$ cross sections at $\hbar\omega = 348.8$ eV and 352.0 eV (see Fig. 2). (b) Theoretical spectra, obtained from the calculated decay rates of the excited $2p^5 3s^2 3p^6 3d4s^2\,{}^3D$ (top) and $2p^5 3s^2 3p^6 3d4s^2\,{}^1P$ (bottom) states to the final states listed in the text by a superposition of Voigt profiles. The ratio of the population of the two excited $2p$-hole states has been set to 1:1.

into the character of the excited states and their decay routes, the autoionizing rates have been calculated perturbatively as described by Cowan.[22] In the initial state the configurations $2p^5 3s^2 3p^6 (3d4s^2$, $3d4p^2$, $3d^2 4s$, and $3d^3)$ were included while in the final state a continuum p electron coupled to the $2p^6 3s^2 3p^4 (3d4s^2$, $3d4p^2$, $3d^3)$ and $2p^6 3s3p^6 (4s^2$, $4s3d$, $4p^2$, $3d^2)$ configurations were considered. The transition rates to configurations with a continuum f electron were found to be much smaller and were neglected in the final calculations. Autoionization strength and energy of 427 transitions have been determined in this way. Autoionization to final states with dominant $2p^6 3s^2 3p^4 3d4s^2$ character have by far the largest probability. The theoretical autoionization spectra displayed in Fig. 3(b) were generated by adding the contributions of all 427 transitions. To simulate the experimental spectrum, all lines were described by a Voigt-profile composed of a convolution of a Lorentzian of 0.5-eV half-width and a Gaussian of 0.85-eV half-width, the Lorentzian taking care of the natural width of the $2p$-$3d$ resonance and the Gaussian of the bandpass of the electron-energy analyzer. The additional broadening due to the finite lifetime of the Ca^+ states caused by the subsequent decay into Ca^{2+} $3p^5 4s$ and $3p^5 3d$ final states was neglected. The energy scale in Fig. 3(b) has been adjusted to the observed position of the Ca $3s$ line. The intensity ratio of the two $2p$-$3d$ resonances has been assumed to be 1:1. Comparing the experimental spectra [Fig. 3(a)] with the calculated spectra [Fig. 3(b)] shows that the characteristic features of the experimental spectra are well reproduced by the calculations. The remaining, easily recognizable, discrepancies between theory and experiment (i) the $3s$ line being too strong relative to the rest of the structure, and (ii) larger splitting of the theoretical pattern than of the experimental, show that further refinements are needed in the theoretical model. It has already been mentioned that a small change in interaction strengths can lead to agreement for the relative strengths of the $2p \rightarrow 3d$ excitations and this will lead to a change in the Auger decay rates as well. The reason behind point (ii) is well known in so far as the calculated splitting of configurations as a rule is larger than the experimental due to neglected interactions with higher configurations. This effect is often taken into account by scaling down the radial integrals.[23] The intensity at the high-energy end of the experimental spectra which is missing in the theoretical ones may in part be due to the neglect of autoionization to $3s3p^5 3d4s^2$ final states which has been calculated to carry 20% of the total strength. This value is consistent with the experimental estimate of 25% for the Ca^{3+} yield.[24]

Our results show that the spectator model breaks down for the $2p$-$3d$ resonances in Ca due to the strength of the $3p$-$3d$ interaction which in turn is due to the collapse of the $3d$ orbital. In particular we note that the inversion of the $3p^4$ parent labels in the $3p^4 3d$ states, first discussed by Cowan,[25] is the main reason for the difference between the decay of the $2p^5 3s^2 3p^6 4s^2$ and $2p^5 3s^2 3p^6 3d4s^2$ configurations. Our results are clear proof that even for resonances involving very deep core holes, the spectator model can break down completely and it should therefore be used with care.

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