Interchannel coupling in the photoionization of the *M* shell of Kr well above threshold: Experiment and theory

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Photoionization cross sections and asymmetry (β) parameters for Kr $3s$, $3p$, and $3d$ subshells have been measured and calculated in the 300–1300-eV photon energy range. Good agreement between experiment and theory is found for both cross-section branching ratios and β parameters. Interchannel coupling among the channels arising from $3s$, $3p$, and $3d$ subshells is found to be necessary for quantitative accuracy of the theory. This shows that the interchannel coupling phenomenology far above threshold, found previously for outer shells of Ne and Ar, is also operative for inner atomic shells.

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I. INTRODUCTION

In the past was it thought that, at photon energies far above thresholds, the single-particle picture describes the photoionization process adequately [1–6]. Recently, however, it has been found that for valence shells, correlation in the form of interchannel coupling is required for adequacy even in this high-energy region [7]. Confirmations of this effect via direct comparison of theory and experiment for the outer $n=2$ shell of Ne [7] and the $n=3$ shell of Ar [8] have been presented. Furthermore, it has been shown that the nonrelativistic high-energy form of the independent-particle photoionization cross section for an atomic nl subshell, $a_{nl}/E^{(7/2+l)}$, is significantly altered by interchannel coupling for all but ns states: for $l=1$, a_{nl} is changed and for $l\geqslant 2$, the exponent is *not* $7/2+l$ but rather 9/2, so that all $l\neq 0$ subshell cross sections behave as $a_{nl}/E^{9/2}$ [9–11].

Theory indicates that this interchannel effect should be operative for outer *and* inner shells, but up to this point there has been no verification for inner shells. In this paper, the situation is remedied. A combined experimental and theoretical study of the Kr $n=3$ subshell cross sections (σ_{3s}, σ_{3p}, and σ_{3d}), along with their photoelectron asymmetry parameters [β_{3p} and β_{3d} ($\beta_{3s}=2$)], have been performed in the 300–1300-eV photon energy region. Brief reviews of the experimental and theoretical methodologies are presented in the next two sections, followed by a presentation and discussion of our results.

Before proceeding, however, it is worthwhile to emphasize that we are dealing with a situation far above thresholds. For low energy, and reasonably close to thresholds, it has been known for some time that correlation in many forms (including interchannel coupling) generally *must* be included for quantitative accuracy [12] and, in many cases, this correlation dominates the cross section [12,13].

II. BRIEF EXPERIMENTAL DETAILS

The experiments were performed at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL) on undulator beamline 8.0 using a gas-phase time-of-flight (TOF) photoelectron-spectroscopy system designed specifically for soft-x-ray work at the ALS. A complete discussion of this apparatus is published elsewhere [14]. A key characteristic for the present measurements is that the TOF method can measure photoelectron peaks at many kinetic energies and at multiple emission angles simultaneously, permitting sensitive determinations of cross-section ratios and electron angular distributions with minimal experimental uncertainty.

III. BRIEF THEORETICAL DETAILS

Calculations have been performed within the framework of the relativistic-random-phase approximation (RRPA) [15,16]. The relativistic single-excitation channels of Kr arising from $3s$, $3p$, $3d$, $4s$, and $4p$ subshells in the photon-energy range from threshold to 1.5 keV were included. Note that in addition to ground-state correlation, as well as two-electron promotions in the Kr-ion cores, the RRPA takes into account interchannel coupling among *all* of the single-excitation final-state channels. The calculation is performed in both length and velocity formulations, which must be equal in RRPA calculations; the equality of our length and velocity results to $\sim 1\%$ demonstrates the numerical accuracy of the calculations, even at such high energies.

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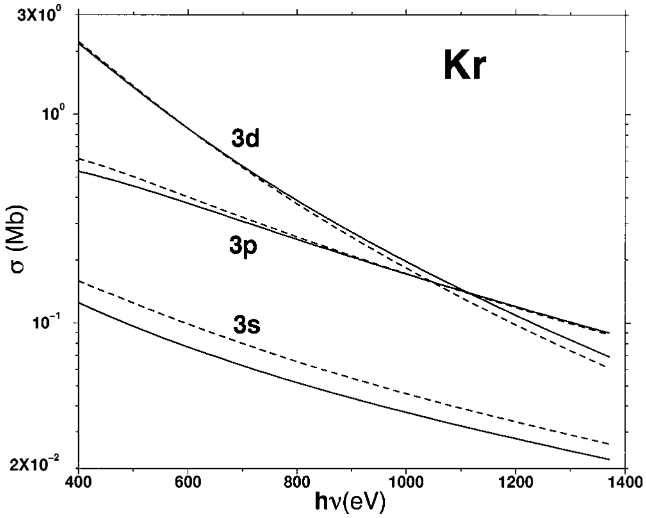

FIG. 1. Photoionization cross sections for the $n=3$ subshells of Kr. The solid lines are the fully coupled RRPA results and the dashed lines are the RRPA results with interchannel coupling between channels arising from different subshells omitted.

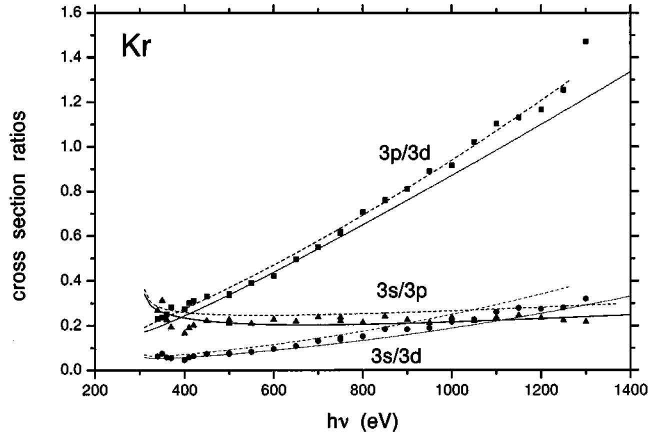

FIG. 2. Ratio among $3s$, $3p$, and $3d$ cross sections of Kr. The points are the present experiment. The solid and dashed curves are the theoretical fully coupled RRPA and RRPA with coupling between channels arising from different subshells omitted.

IV. RESULTS AND DISCUSSION

Our theoretical results for the $3s$, $3p$, and $3d$ subshell cross sections are shown in Fig. 1. For each subshell, two cross sections are shown: the full RRPA cross section, which includes interchannel coupling among all single-excitation channels arising from $3s$, $3p$, $3d$, $4s$, and $4p$ subshells; and RRPA without coupling among channels arising from different subshells. In the low-energy portion of the curve, σ_{3d} dominates, while on the high-energy side, σ_{3p} is largest. Over the entire range shown, however, σ_{3s} is smaller than the other two $n=3$ cross sections by approximately an order of magnitude.

In addition, it is clear from Fig. 1 that interchannel coupling among channels arising from different subshells produces the largest change for the smallest cross section, σ_{3s}, decreasing it by approximately 30%. Furthermore, small changes in σ_{3p} are seen, due to interchannel coupling, when σ_{3d} is significantly larger than σ_{3p}. Where σ_{3p} dominates, small changes in σ_{3d} are seen due to the interchannel coupling. In the former case a decrease is seen, as in the $3s$ case, while in the latter case, interchannel coupling increases the cross section.

This behavior can be understood in much the same manner as the outer shells previously studied [7,8] in terms of simple perturbation theory ideas. Briefly, the wave functions of the final (continuum) states are perturbed by each other, so that the ''true'' wave function is a mixture, a linear combination, of the wave functions of all possible states (a complete set) [17]. This mixing, known as interchannel coupling, is simply configuration interaction in the continuum, so that the traditional sums over discrete states become integrals over continuum states [17]. From perturbation theory, the mixing coefficient is just the interchannel coupling Coulomb matrix element over the energy denominator. When the dipole transition matrix element from the initial state to a particular unperturbed final state is small, a small admixture with an unperturbed state that has a large dipole transition matrix element can substantially modify the small dipole matrix element for the transition to the original unperturbed state. This argument makes it clear that channels with small transition amplitudes (cross sections) will be modified by admixture with channels having large amplitudes, but those with large amplitudes will be relatively unaffected by this mixing, exactly as seen in Fig. 1. Of course the sign of the correction depends upon the sign of the mixing coefficients, which can be positive or negative, so it is not possible *a priori* to predict if the interchannel coupling correction will increase or decrease the cross section.

The general form of the interchannel coupling matrix element among the final states arising from a $nl^q n'l'^p$ initial state is $\langle nl^{q-1}n'l'^p \epsilon l_f | H-H_0 | nl^q n'l'^{p-1}\epsilon' l'_f\rangle$, where H and H_0 are the total and unperturbed Hamiltonians, respectively, which reduces to $\langle n'l'\epsilon l_f | e^2/r_{12} | nl\epsilon' l'_f\rangle$. For this matrix element to be significant over a broad energy range, there are two requirements: first, it is necessary that $n=n'$ so that the discrete functions occupy the same region of space and their overlap is large; and second, the binding energies of the discrete states must be similar so that for a given $h\nu$, ϵ, and ϵ' are close to each other resulting in *constructive* interference of the continuum waves over a broad energy range. These considerations show that, in the present case, coupling among all of the photoionization channels must be taken into account to obtain an accurate picture of the photoionization process.

Our theoretical and experimental results for the cross-section ratios σ_{3s}/σ_{3p}, σ_{3s}/σ_{3d}, and σ_{3p}/σ_{3d} are shown in Fig. 2. Comparisons of ratios are investigated, rather than the individual cross sections, because most experimental uncertainties cancel out in the ratios, rendering them much freer from systematic errors than the cross sections themselves. Error bars are omitted from Fig. 2 for clarity. The size of the error bars depends on the statistical error of the peak areas and the ''tails'' of the satellite peaks overlapping with the

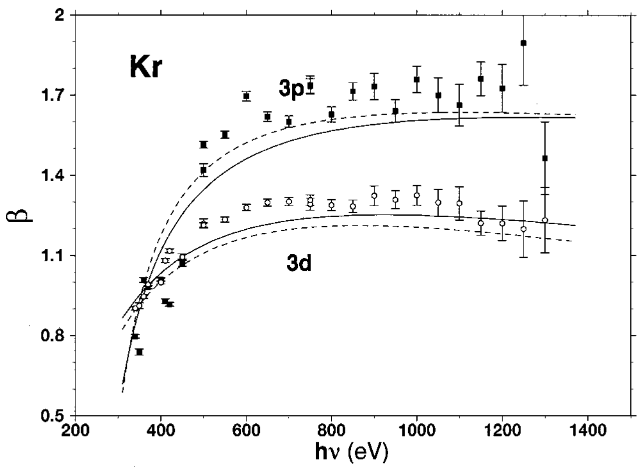

FIG. 3. Photoelectron angular distribution parameter β for the $3p$ and $3d$ subshells of Kr. The points are the present experiment. The solid and dashed curves are the theoretical fully coupled RRPA and RRPA with coupling between channels arising from different subshells omitted.

main lines. Below 400 eV are some photon energies where partial overlaps of the $3s$ main line and Auger lines occur, thus increasing the error bars there to up to ± 0.05. Otherwise, the error bars range between ± 0.02 at 400 eV, ± 0.03 at 800 eV, and ± 0.04 at 1200 eV for all ratios. The energy resolution was kept constant by employing a retarding voltage offsetting the photon energy increase, thus keeping the final kinetic energy of the photopeaks constant. The satellite lines were always separate from the main lines and the energy resolution was never more than 4 eV, i.e., for $3d$ at 1300 eV, and as good as 1 eV for the $3s$ subshell at 400 eV. The photon beam resolution was always better than 1000 $(E/\Delta E)$ and did not contribute significantly to the total energy resolution.

It is clear from Fig. 2 that the ratios involving σ_{3s} show excellent agreement between the fully coupled RRPA calculation and the experimental points; experiment clearly favors the fully coupled theory over the uncoupled. This indicates both that the interchannel coupling is of importance and that the theory does indeed treat the interchannel coupling correctly, particularly for the $3s$ cross section where it is an appreciable effect. Surprisingly, however, for the σ_{3p}/σ_{3d} ratio, where interchannel coupling was seen to be a much smaller effect than in the ratios involving σ_{3s}, experiment is in roughly as good agreement with the fully coupled theoretical result as the uncoupled result. We have no explanation for this result, since we believe that the experimental points are well characterized, as discussed above, and the theory includes all of the major interactions affecting these cross sections. To pin this down will require further study.

The results for the photoelectron angular distribution asymmetry parameter β for Kr $3p$ and Kr $3d$ are shown in Fig. 3. A comparison between the coupled and uncoupled theoretical results shows that interchannel coupling is relatively unimportant here. There are two reasons for this. First, as seen from the cross sections of Fig. 1, interchannel coupling is a rather small percentage effect for $3p$ and $3d$. Second, β is itself a ratio [18] and the interchannel effects, such as they are, tend to cancel. Comparison with our experimental results, also shown in Fig. 3, reveals good (but not spectacular) agreement between theory and experiment for both $3p$ and $3d$. In any case, the situation here is rather like the case of Ar $3p$ [8], where β was only marginally affected by interchannel coupling.

V. CONCLUDING REMARKS

It has been shown that, even far away from thresholds, interchannel coupling among photoionization channels arising from the inner $n=3$ shell of Kr remains important. In particular, this interchannel coupling significantly modifies the cross sections of the weaker channels through the mixing of their wave functions with the wave functions of the stronger channels. This modification can be manifested as an increase or a decrease in the cross section of a weak channel, depending upon the relative phases of the direct (zeroth-order) dipole matrix element and the correction induced by interchannel coupling. Thus, the phenomenology is exactly the same as found for outer shells [7,8].

Furthermore, good agreement was found between our experimental results and our fully coupled theoretical results for the subshell cross-section ratios involving the $3s$ subshell where the largest manifestation of interchannel coupling was found; the deviation from experiment of the theoretical ratios with interchannel coupling omitted was also demonstrated in these cases. The photoelectron angular distribution parameter β for $3p$ and $3d$ ionization turned out to be only rather weakly perturbed by interchannel coupling, and our experimental results are in similar agreement with both coupled and uncoupled calculations. This is much the same situation as found previously for Ar $3p$ [8].

Of particular importance is that the interchannel effects found for the $n=3$ inner shell of Kr should be qualitatively representative of all inner shells with multiply occupied subshells. Thus, the present inner-shell results, plus the previous results for outer shells [7,8], lead us to the conclusion that these interchannel effects should be qualitatively reproduced for *any* shell, inner or outer, with multiply occupied subshells, for any atom, ion, molecule, cluster, surface, or solid. The details will vary, depending upon the particular case, but the fundamental phenomenology should manifest itself generally, even at high energies far from thresholds.

Finally, it is of interest to speculate how these results might apply to the photoionization of positive atomic ions. Going along an isoelectronic sequence, for example, the nuclear attraction increases relative to the interelectron interactions. Since it is the interelectron forces that are responsible for correlation, including interchannel coupling, it seems reasonable to predict that this interchannel coupling effect will decrease in importance as nuclear charge Z increases along the sequence. Theoretical studies of ionic photoionization are in progress to elucidate the details of the evolution of this interchannel coupling effect along isoelectronic sequences.

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