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Kr $3d_{5/2}$:$3d_{3/2}$ branching ratio from 97 to 200 eV

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The Kr $3d_{5/2}$:$3d_{3/2}$ branching ratio has been measured between 97 and 200 eV photon energies using monochromatized synchrotron radiation from the Tantalus storage ring. The branching ratios have been obtained both from the Kr $3d_{5/2,3/2}$ photolines, and from the Kr $M_{4,5}N_1N_{2,3}$ ($^1P_1$) Auger lines in the low- and high-photon-energy ranges where the direct photoelectron measurements are very difficult. The agreement between results for the two methods is very good. In contrast with the Xe $4d_{5/2}$:$4d_{3/2}$ branching ratio, the Kr $3d_{5/2}$:$3d_{3/2}$ ratio is almost a constant and very close to the statistical value of 1.5 throughout the energy range studied. Our results are not in good agreement with the theoretical relativistic random-phase approximation results which predict a variation of the $3d_{5/2}$:$3d_{3/2}$ ratio of 1.4–1.7 between 100 and 120 eV, due to an initial decrease in $3d$ cross sections to 105 eV followed by a slow increase. Our results show that the $3d$ cross sections increase immediately above threshold.

I. INTRODUCTION

The Xe $4d_{5/2}$:$4d_{3/2}$ branching ratio has been studied experimentally and theoretically between 74 and ~ 180 eV photon energies by a number of authors.[1–10] The branching ratio deviates greatly from the statistical value of 1.5, especially near threshold. For example, the branching ratio decreases rapidly from 3.2 eV at 74 eV to 1.13 eV at 84 eV, and then increases to 1.34 at 94 eV before decreasing very slowly to 1.22 at 146 eV.[10] The experimental results are in good semiquantitative agreement with the latest theoretical relativistic random-phase approximation (RRPA) calculations.[9]

The above Xe results, and the recent publication of theoretical RRPA calculations of Kr $3d_{3/2,5/2}$ cross sections,[11] between 103 and 136 eV, made the analogous Kr $3d_{5/2}$:$3d_{3/2}$ branching ratios interesting to determine. Although the total Kr $3d$ cross sections have been obtained from photoabsorption measurements,[12] there does not appear to be any photoelectron measurements of the individual $3d_{5/2}$ and $3d_{3/2}$ cross sections or the $3d_{5/2}$:$3d_{3/2}$ branching ratio. Three effects make these Kr measurements much more difficult than those for the analogous Xe $4d_{5/2,3/2}$ levels. First, the Kr $3d$ cross section is generally much lower than the Xe $4d$ cross section, from threshold to 150 eV. For example, the maximum Xe $4d$ cross section of ~ 30 Mb is about five times the maximum Kr $3d$ cross section.[12] Second, the Kr $3d$ spin-orbit splitting (1.22 eV) (Ref. 13) is much smaller than the Xe $4d$ value (1.98 eV).[1,10] Third, the overlapping Kr $M_{4,5}NN$ Auger peaks extend over a wide energy range (10–60-eV kinetic energy) compared with the 10–35-eV kinetic energy range for the Xe *NOO* Auger lines.[14]

In this paper we report precise measurements of the Kr $3d_{5/2}$:$3d_{3/2}$ branching ratio from just above threshold (97 eV) to 200 eV using both the Kr $3d$ photolines and the $M_{4,5}NN$ Auger peaks. Somewhat surprisingly, the branching ratios are rather constant at 1.5; they differ even qualitatively from the analogous Xe $4d_{5/2}$:$4d_{3/2}$ values, and they are not in agreement with recent RRPA calculations.

II. EXPERIMENT

The measurements were carried out using the Canadian Synchrotron Radiation Facility at the Tantalus storage ring in Stoughton, Wisconsin, as described in a recent paper.[10] In the present study, a 600 lines/mm holographic grating from JY, Inc. was used in our Grasshopper Mark IV monochromator, along with entrance and exit slit widths between 75 μm (0.6-Å resolution) and 150 μm (1.3-Å resolution). Either 50- or 100-eV pass energy was used for the Leybold-Heraeus electron analyzer, giving an electron spectrometer contribution to the observed linewidths of 0.4 and 0.6 eV, respectively.

As stated in our previous paper,[10] the transmission of the lens analyzer is almost constant from ~ 8- to ~ 34-eV kinetic energy. Using Werme's Kr *MNN* normalized Auger intensities,[14] we have further confirmed that our transmission varies by less than 20% from 10–60-eV kinetic energies. Thus, for the 1.22-eV kinetic energy difference between the $3d_{5/2}$ and $3d_{3/2}$ lines, or the $M_5N_1N_{2,3}$ and $M_4N_1N_{2,3}$ lines, the difference in transmission is less than 1% and can be neglected. At lower kinetic energies, where the transmission function may well vary more, there is an obvious advantage in deriving the branching ratios from the $M_{4,5}N_1N_{2,3}$ Auger lines whose kinetic energies of ~ 40 eV (Fig. 1) are independent of photon energy. The Auger-derived branching ratios are thus independent of the transmission function of our lens/analyzer.

All spectra were fitted to combination Lorentzian-Gaussian peak shapes using an iterative procedure derived earlier.[15] The widths and Gauss fractions of the spin-orbit components were constrained to be equal. Standard deviations on the computed branching ratios were generally less than 0.07, and we have shown previously from detailed statistical analyses[10] that these errors are realistic.

III. RESULTS AND DISCUSSION

A typical Kr $3d$ photoelectron spectrum at 130-eV photon energy, 50-eV pass energy, and 75-μm monochromator slits

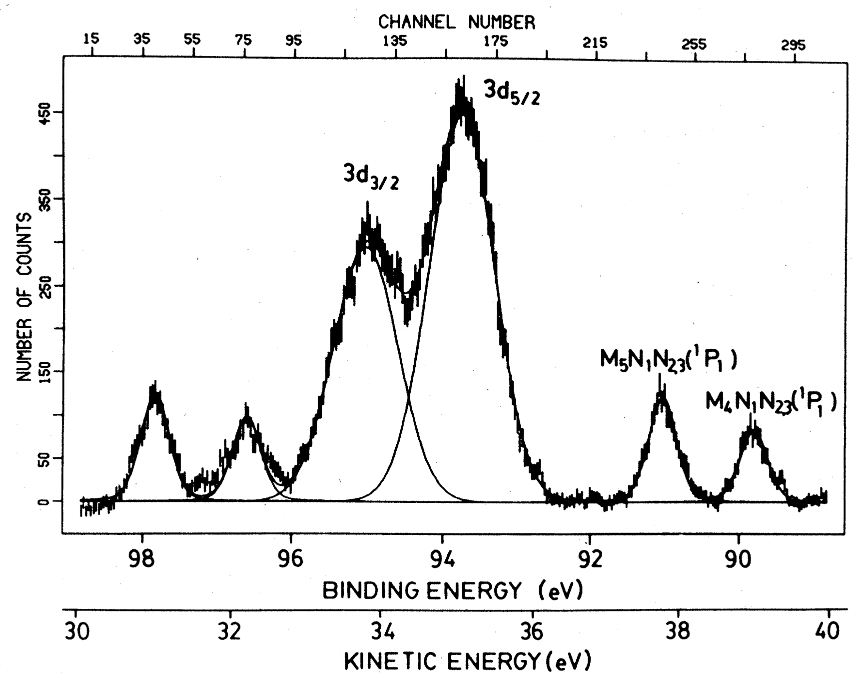

FIG. 1. The Kr $3d$ and part of the *MNN* Auger spectrum taken at 130-eV photon energies, 75-μm slits, and 50-eV pass energy.

is shown in Fig. 1. At this energy, the Kr $3d_{5/2}$ cross section is about 1.6 Mb,[11] and count rates of ~ 20 counts/s for 150-mA storage ring beam current were obtained. In addition to the dominant Kr $3d_{5/2}$ and $3d_{3/2}$ photolines, *MNN* Auger peaks are also apparent on both high- and low-energy sides of the $3d_{5/2,3/2}$ lines. The two peaks at low binding energy (kinetic energy of 40 eV) are readily identified as the $M_{4,5}N_1N_{2,3}$ ($^1P_1$) Auger lines,[14] and their areas are about 14% of the areas of the corresponding $3d$ photolines. The total width of the Kr $3d$ peaks and the Auger peaks are 1.0 and 0.45 eV, respectively.

The Auger peaks in Fig. 1, the low count rates, and 1-eV widths indicate the problems of using the $3d$ peaks to measure the branching ratios at low and high kinetic energies, respectively. Except in "window" regions of the Auger spectrum, the Auger peaks make it difficult to use the $3d$ peaks between 10 and 60 eV. At kinetic energies above 40 eV, the count rates for a constant 1.0-eV width decrease greatly for two reasons. First, the monochromator slit widths have to be decreased, and second, the intensity from the Tantalus ring is dropping sharply.[10] Therefore, we have normally used the well-resolved $M_{4,5}N_1N_{2,3}$ Auger lines for the branching-ratio determinations, because their width is independent of the photon energy and slit width.

Figure 2 shows the branching ratios obtained in this study. The intensity ratio obtained from the Auger peaks is

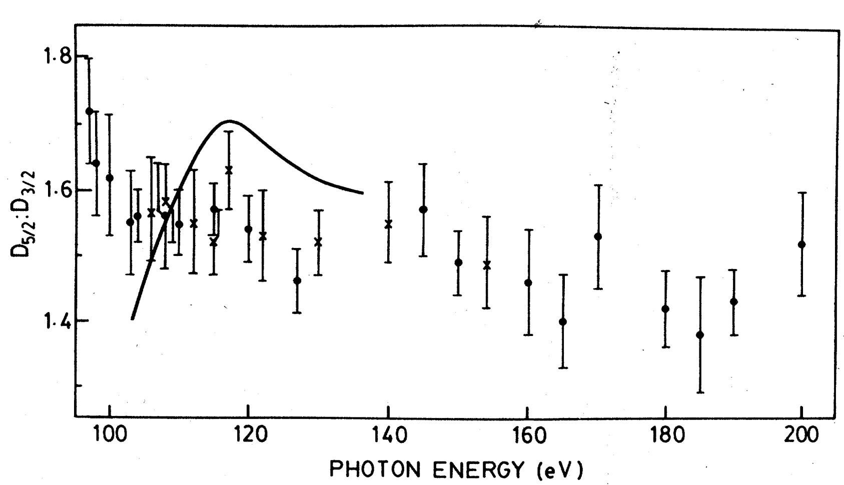

FIG. 2. The Kr $3d_{5/2}$:$3d_{3/2}$ branching ratio as a function of photon energy from 97–200-eV photon energies: ●, from the $M_5N_1N_{2,3}$:$M_4N_1N_{2,3}$ area ratio; ×, from the $3d_{5/2}$:$3d_{3/2}$ area ratio. The solid curve shows the theoretical values from Huang, Johnson, and Cheng (Ref. 11).

not necessarily the same as that obtained from the $3d_{5/2}$:$3d_{3/2}$ ratio, because the intensity distribution between different line components could be different in the M_4 and M_5 line groups. However, the duplicate results at 108 and 115 eV show that the two ratios are in good agreement. Good agreement between the Xe $4d_{5/2}$:$4d_{3/2}$ and I_{N_5OO}/I_{N_4OO} intensity ratios was also found for Xe,[5,10] showing that the Auger ratios can be used to accurately determine the photoelectron branching ratios.

In contrast with the Xe $4d_{5/2}$:$4d_{3/2}$ branching ratios, the Kr $3d_{5/2}$:$3d_{3/2}$ branching ratios in Fig. 2 are remarkably constant, about 1.5, even very near threshold. The rather small Kr $3d$ spin-orbit splitting minimizes changes in the branching ratio, but the Kr $3d_{5/2}$:$3d_{3/2}$ behavior is still fundamentally different than that of the Xe $4d_{5/2}$:$4d_{3/2}$ ratio. These differences can be understood using the calculated cross-section curves[11] and the branching ratios that we obtained from them (plotted in Fig. 2). The Kr $3d$ cross section turns on very slowly—much slower than the Xe $4d$ cross section— due to the well-known delayed onset from the angular momentum barrier.[12] Indeed, the calculated cross sections[11] actually decrease from threshold to ~ 105 eV before increasing slowly to a maximum at 200 eV.[12] As pointed out by Walker and Waber,[16] and shown in the theoretical branching ratio, the *decrease* in cross sections just above threshold (< 105 eV) gives a predicted branching ratio of less than 1.5. Instead, we observe a value just *greater* than 1.5 below 105 eV strongly indicating that the Kr $3d$ cross sections *increase* very slowly above threshold. Our branching ratios are thus a very sensitive way of determining the $3d$ cross-section behavior just above threshold. This discrepancy between theory and experiment near threshold is probably not surprising. As pointed out for the Xe $4d$ levels,[10] correlation and relaxation effects are important near threshold and are very difficult to calculate.

Somewhat above threshold, the theoretical results indicate that the branching ratio should increase from 1.4 at 104 eV to 1.7 at 115 eV. Additional spectra at these energies improved our statistics, and gave branching ratios of 1.56 ± 0.04 at 104 eV and 1.57 ± 0.04 at 115 eV. These results confirm that the $3d$ cross sections do not show a minimum at ~ 105 eV. Above these energies (to about 160 eV), the slow increase in the Kr $3d$ cross section, combined with the small $3d$ spin-orbit splitting, keeps the branching ratio at, or just above, 1.5. Near or beyond the cross-section maximum at 200 eV, the branching ratio would be expected to decrease slightly, as observed.

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