Measurement of the spin-orbit branching ratios and the angular asymmetry parameter in the region of the $4s\,4p^6\,5p$ resonances in krypton and the $5s\,5p^6\,6p$ resonances in xenon

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Variation of the ratio of partial photoionization cross sections $R=\sigma(^2P_{3/2})/\sigma(^2P_{1/2})$ and the asymmetry parameter β have been determined in the region of the $4s\,4p^6\,5p$ resonances in krypton and $5s\,5p^6\,6p$ resonances in xenon. In both cases these resonances are affected by the interaction with a configuration involving two excited outer p electrons. This admixture influences the number of resonances present, and the value of β and R. Large variations in β and R are observed in the region of these resonances.

I. INTRODUCTION

The rare gases have provided an important testing ground for the development of new and more sophisticated experimental[1] and theoretical[2] techniques to study the dynamics of the photoionization process. Total and partial cross sections have been measured,[3] and techniques have been developed to study β, the parameter governing the angular distribution,[4–7] and spin polarization parameters of the ejected electrons.[8] Several formalisms have been developed to deal with the problem of accounting for correlation in the photoionization process and to obtain accurate cross sections. A representative selection is close coupling,[9] R matrix,[10,11] random-phase approximation (RPA),[12,13] relativistic random-phase approximation (RRPA),[14] and the many-body formalism.[15–17] The angular-momentum-transfer formalism[18] and the quantum-defect theory[19] were combined to chart the angular distribution parameter and cross-section variation[20] as a function of photon energy near autoionizing resonances. More recently, RRPA (Ref. 14) was combined with multichannel quantum defect theory (MQDT)[21] to compute[22] all the photoionization parameters for the noble gases near threshold.

Only recently[23,24] have high-throughput, high-resolution monochromators been available at synchrotron sources for stepping through resonances and for obtaining branching ratios, the angular asymmetry parameter β and the polarization parameters ξ,η,ζ, of the ejected photoelectrons. The first measurement of the variation of the angular distribution of ejected photoelectrons in the region of autoionizing resonances was made by Samson and Gardner[25] between the $^2P_{3/2}$ and $^2P_{1/2}$ ionization limits of xenon. Later Heinzmann *et al.*[23] determined the polarization parameters for photoelectrons in this same photon energy region. Kemeny *et al.*[26] measured the variation of the branching ratio $\sigma(^2P_{3/2})/\sigma(^2P_{1/2})$ in the vicinity of the inner-shell autoionizing resonance of xenon[27] due to the transition $5s^25p^6\,{}^1S_0\rightarrow 5s\,5p^6 6p$. More recently, Codling *et al.*[28] extended this work to argon and measured the angular distribution parameter β as well. In molecules the branching ratio and β have been measured for vibrationally resolved final ionic states of autoionizing resonances in O_2,[29] N_2,[30] and CO.[31]

The results we present here are a continuation and extension of earlier measurements[28] of β values and branching ratios in the vicinity of resonances in argon and xenon. The present measurements of

β and the branching ratio have been obtained in the vicinity of the lowest inner-shell Rydberg states of krypton and xenon, corresponding to transition $ns^2np^6\,{}^1S_0 \rightarrow nsnp^6(n+1)p\,{}^1P_1$ in pure LS coupling. The quantity n is equal to 4 or 5 for the case of krypton or xenon, respectively. These excitation states are interesting candidates for detailed study from several points of view. Firstly, the resonances decay by autoionization into the adjacent ϵs and ϵd continua, and branching ratio and β measurements provide information about the decay of resonances into these adjacent continuum channels. Secondly, the coupling for these states changes from almost pure LS coupling to intermediate coupling as one proceeds from argon to xenon. Thirdly, in the energy interval of these one-electron excitation states there are two-electron excitation states owing to transitions of the type $ns^2np^6\ {}^1S_0 \rightarrow ns^2np^4n'1'n''1''(J=1)$. These resonances interact or overlap with the one-electron excitation states. In order to understand the couplings theoretically, it is essential to have as much information as possible about the parameters that describe the interaction. Fourthly, the rare gases are a closed-shell system and there are powerful computational techniques available[18–22] to study the coupling mechanisms of these atoms. New experimental information about these resonances will provide the motivation to study these resonances by these theoretical techniques. This series of measurements of key photoionization parameters in the vicinity of autoionizing resonances provide, for example, a new challenge for the development of MQDT in the frame work of RRPA.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

For the present measurements, a 2-m high throughput normal-incidence monochromator[24] was used with the SURF-II 250-MeV storage ring at the National Bureau of Standards. The 100-μm high electron beam was the entrance slit, and with 100-μm exit slits the 1200-lines/mm osmium coated grating yielded fluxes of 10^{10} photon/s in the 0.5-Å bandwidth at typical ring operating currents of 10–15 mA. A 2-mm diameter by 200-mm long capillary was attached to the slit to provide channeling for the monochromatized synchrotron radiation and to provide a high impedance path between the ultrahigh vacuum (10^{-9}-torr base pressure) of the monochromator and the rather low vacuum in the ($10^{-5}-10^{-4}$ torr with sample) sample chamber. The photons interact with the rare gas sample and the ejected photoelectrons are analyzed by a 50-mm mean radius hemispherical electron spectrometer.[32] The electron analyzer is rotatable in a plane perpendicular to the photon propagation direction. The analyzer was operated at a constant pass energy of 5 eV and had a bandpass of about 0.1 eV at this energy. The relative efficiency of the lens system in the spectrometer was carefully calibrated using the known total photoabsorption cross section of argon.[33]

The electron counting rate $N(\theta,\lambda,E)$ at wavelength λ, kinetic energy E, and the angle θ between the polarization direction and the electron emission direction is given by

$$N(\theta,\lambda,E)=I(\lambda)K(\theta,E)\sigma_i(\lambda) \times\{1+\beta_i[3p(\lambda)\cos2\theta+1]/4\}/4\pi\ , \quad (1)$$

where $I(\lambda)$ is the output flux of the monochromator at wavelength λ, $\sigma_i(\lambda)$ is the partial cross section in the ith channel, $K(\theta,E)$ is a constant related to the pressure, the solid angle, the electron kinetic energy E, and source volume of the electron spectrometer. The quantity β_i is the angular asymmetry parameter for channel i, and p is the photon polarization. The polarization was continuously monitored during the course of these measurements by a three-mirror polarization analyzer[32] and the quantity $K(\theta,E)$ was measured relative to $\theta=0$ by carefully calibrating the angular response of the electron spectrometer using the best available determinations[34,35] of the asymmetry parameter in argon. This correction was typically less than 4% in the worst case.

For each photon energy in the vicinity of the resonances the electron count renormalized to the photon flux was obtained at three angles: 0°, 45°, and 90°. From the electron kinetic energy, the values of $K(\theta,E)$ and p, the asymmetry parameter was determined at θ equal to 45° and 90°. The branching $R=\sigma({}^2P_{3/2})/\sigma({}^2P_{1/2})$ could be obtained from the value of β and from the sum S of the angle-corrected integrated electron count at 0°, 45°, and 90° for the two final ionic states. The expression for R in terms of these quantities is

$$R=\frac{S({}^2P_{3/2})[1+\frac{1}{4}\beta({}^2P_{1/2})]}{S({}^2P_{1/2})[1+\frac{1}{4}\beta({}^2P_{3/2})]}\ . \quad (2)$$

The error bars shown on the figures are an estimate of the statistical errors due to the variation of the quantities β or R when evaluated from the data obtained for $\theta=45°$ or $\theta=90°$ relative to $\theta=0°$.

The values of β and R vary rapidly in the vicinity of these resonances, and small electron beam motion in the storage ring can induce wavelength changes that would cause additional scatter in the value of β and R near the resonance. The fine line through the data points associated with β or R is intended only to guide the eye through the variations of these quantities of the resonance region.

III. EXPERIMENTAL RESULTS AND DATA

The values obtained for the krypton and xenon asymmetry parameters are shown at the bottom of Figs. 1 and 2. The value of β associated with the two ionic final states $^2P_{3/2}$ and $^2P_{1/2}$ are plotted as closed circles and triangles, respectively, and with the ordinates displaced by unity for clarity. The total cross section[36] σ_T is plotted at the top of each figure so that variation in the cross section can be compared with variations in the β values. The open circle and triangle in Fig. 1 is the result obtained by Holland *et al.*[34] near this resonance and is consistent with the present measurements.

In Fig. 2, the present results for β are shown as the closed circles and triangles for the xenon ionic states $^2P_{3/2}$ and $^2P_{1/2}$, respectively. The single open circle and triangle at 21.2 eV is a point where recent measurements of Holland *et al.*[34] overlap the present measurements in the resonance region. The other open circles and triangles between 20.8 and 21.1 eV are the earlier results obtained by Codling *et al.*[28] for the most prominent resonance at 20.95 eV. The present results are in good agreement with the data of Codling *et al.*

Codling *et al.*[28] found β to be the same for both final electronic states of the ion in the neighborhood of the argon $3s^2 3p^6\,{}^1S_0 \rightarrow 3s3p^6 4p\,{}^1P_1$ resonance. In Figs. 1 and 2, the variation of β associated with the two ionic states near the resonance is very different in contrast to the results obtained for argon. Three important interactions clearly influence the behavior of β for krypton and xenon. The first is the spin-orbit interaction and the second is the presence of two-electron excitation states involving the promotion of two outer p electrons. Finally, there can be an interchannel interaction that couples the two-electron excitations with the inner shell resonance. The resonance profile of argon is that of an isolated resonance because the spin-orbit interaction is small and there are no two-electron excitation states nearby in energy.

Under strict LS selection rules, only the transition between the $^1S_0$ initial state and the final state of symmetry $^1P_1$ would be permitted, but as the

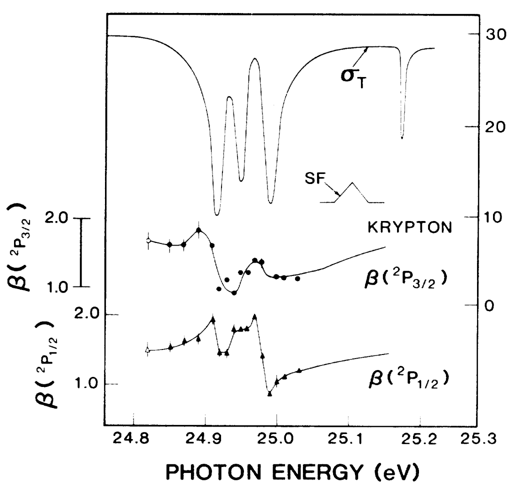

FIG. 1. Angular asymmetry parameter β for the $^2P_{3/2}$ (●) and $^2P_{1/2}$ (▲) ionic states in krypton plotted with a displaced ordinate as a function of photon energy. Symbols ○ and △ are data from Ref. 34. Thin line through the data points is hand drawn to guide the eye. Total cross section σ_T plotted in the upper half of the figure is from Ref. 36. SF is a triangular slit function of 0.5-Å FWHM.

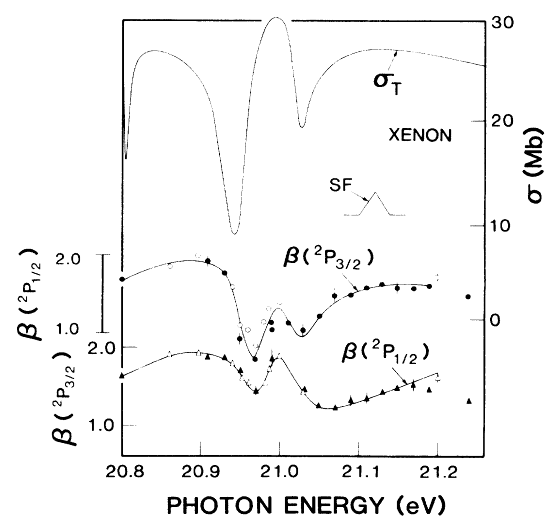

FIG. 2. Angular asymmetry parameter β for the $^2P_{3/2}$ (●) and $^2P_{1/2}$ (▲) ionic states in xenon plotted with displaced ordinates as a function of photon energy. Symbols ○ and △ at 21.2 eV are data from Ref. 34. Symbols ○ and △ between 20.8 and 21.05 eV are from Ref. 28. Thin line through the data points is hand drawn to guide the eye. Total cross section σ_T plotted in the upper half of the figure is from Ref. 36. SF is a triangular slit function of 0.5-Å FWHM.

spin-orbit interaction increases, $^1P_1$ and $^3P_1$ become mixed and transitions to the $J=1$ levels of both the singlet and triplet terms would be allowed. We have estimated the extent of this mixing in the $nsnp^6(n+1)p$ configuration of argon, krypton, and xenon by a Hartree-Fock (HF) calculation.[37] In argon, the coupling is over 99% LS and only the $^1P_1$ transition is expected and observed with any intensity because of the absence of the other two-electron interactions. In the case of krypton, the spin-orbit interaction is still much smaller than the exchange interaction and $L\cdot S$ coupling is a good approximation in the absence of other interactions. However, in krypton for the photon energy range shown in Fig. 1 (24.8 – 25.3 eV) there are five resonances (one at 24.84 eV is not shown), and at most two can be associated with the one-electron transition. In xenon, the spin-orbit term is similar in size to the exchange term and the coupling is becoming intermediate, but the wave function is still 88% $^1P_1$. Nevertheless, in xenon between 20.8 and 21.2 eV there are three resonances, and only one of these (the one at 20.95 eV) has been classified[27] as a member of the one-electron excitation spectrum. The almost pure $L\cdot S$ coupling of the terms of the $nsnp^6(n+1)p$ configuration in krypton and xenon and the presence of several nearby resonances in the xenon and krypton spectrum suggest that the terms of $nsnp^6(n+1)p$ configuration couple strongly with the terms of the configuration involving the excitation of two outer p electrons, and the wave function describing these resonances are at least an admixture of terms of the $nsnp^6(n+1)p$ configuration and of $np^4n'1'n''1''$ configuration. It is clear that any theoretical interpretation of the resonance in this spectral region must include the two-electron excitation states as a part of the basis set. These detailed measurements of the asymmetry parameter β will provide input for new calculations to separate the spin-orbit interactions from the two-electron configuration interaction and the correlation in these important test cases.

Besides information about the variation of the asymmetry parameter β through the energy range of a resonance, complimentary information has been obtained by determining the branching ratio R between the photoionization cross section $\sigma(^2P_{3/2})$ and $\sigma(^2P_{1/2})$ through this resonance region. In Figs. 3 and 4, the results for R are presented in the lower portion of the figure for krypton and xenon, respectively. The variation of R can be compared with the total cross section[36]

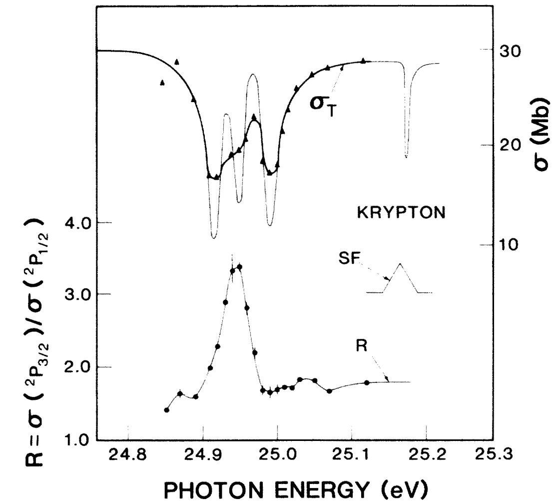

FIG. 3. Ratio R of the krypton partial cross section $\sigma(^2P_{3/2})$ to $\sigma(^2P_{1/2})$ as a function of photon energy. Thin line through the data points (●) is hand drawn to guide the eye. Total cross section σ_T in the upper half of the figure was obtained from Ref. 36. Heavy line is the convolution of σ_T with SF, the triangular slit function. Data (▲) are the total cross sections obtained by a method outlined in the text.

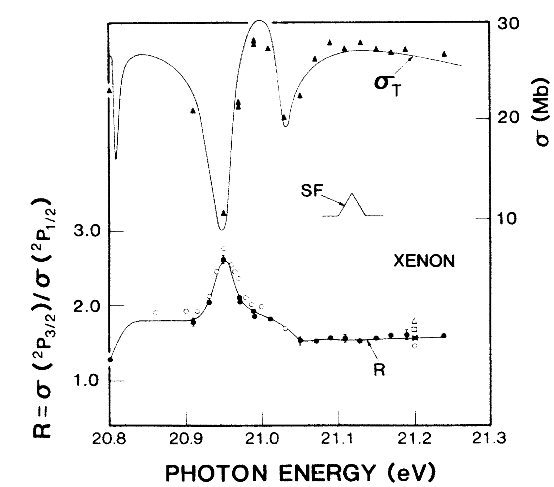

FIG. 4. Ratio R of the xenon partial cross section $\sigma(^2P_{3/2})$ to $\sigma(^2P_{1/2})$ as a function of photon energy. Thin line through the data points (●) is hand drawn to guide the eye. Points ○ between 20.8 and 21.05 eV were obtained from Ref. 28. Symbols, △, □, ○, × at 21.2 eV are from Refs. 41, 40, 39, and 38, respectively. Total cross section σ_T in the upper half of the figure was obtained from Ref. 36. Data (▲) was obtained by a method outlined in the text.

which is plotted in the upper part of the figure. For krypton, the total cross section, shown as the light line in Fig. 3, was convoluted with a triangular slit function of 0.5 Å fullwidth at half maximum (FWHM). The result of this convolution is the heavy curve shown in the top of the portion of the figure. To compare our results with this convolution, the total cross section has been reconstructed from the relative partial cross sections by normalizing the data to the same pressure and to the total cross section at one wavelength. These results have been plotted as solid triangles in the upper frame of Figs. 3 and 4 for krypton and xenon, respectively. A similar convolution for xenon by Codling *et al.*[28] only affected the cross section minimum, but since the krypton resonances are narrower than the xenon resonance the effect of the 0.5-Å bandpass is more pronounced in krypton. The properly normalized total cross sections obtained from the branching ratio R and β are in good agreement with the convoluted cross section.

The branching ratio for krypton is shown in the lower portion of Fig. 3. The present value of R in the wings of the resonance is in good agreement with the earlier measurements of Samson *et al.*[38] (Samson obtained a constant value of $R = 1.77$ for 14.7 eV $\leq h\nu \leq$ 40.8 eV.) In the lower portion of Fig. 4, the present data of R for xenon are shown as filled-in circles. The earlier data of Codling *et al.*[28] are the open circles, and the earlier results of Kemeny *et al.*[26] in the resonance region are not shown but are in fair agreement with the present results. The open circle, open square, and open triangle at 21.2 eV is the result obtained by Krause *et al.*,[39] Wuilleumier *et al.*,[40] and Levinson *et al.*,[41] respectively. The point obtained by Samson *et al.*[38] is indicated by the $\times$. The present value lies within the error limits of the other measurements, but the data obtained at this point by the various authors have a fairly large variation. It has been suggested[40] that the large known electron scattering cross section in xenon would affect the branching ratio by scattering the electrons originating from the two ionic states differently. This is particularly true for electrons of low kinetic energy produced near the photoionization threshold. In the present apparatus, the total path length was short (about 30 cm), the pressure was maintained at $(2-3)\times 10^{-5}$ torr, and the kinetic energy of the electrons traversing the analyzer was the *same* for the electrons of both ion states. Furthermore, changing the pressure did not affect the derived value of R. The conclusion we draw is that in this energy range for our analyzer, electrons originating from either ion state are scattered negligibly and with about the same probability, and that for these measurements, electron scattering from xenon is not an important source of systematic error.

The ratio of the partial cross sections R for argon was found[28] to be a constant for the inner-shell resonance. The results shown in Figs. 3 and 4 show this is clearly not the case for krypton and xenon. The large value (3.5) of R at 24.95 eV for krypton is an indication that the resonances at 24.92 and 24.99 eV decay to both ionization channels to the same extent, but that the resonance at 24.95 eV decays *almost entirely* to the open channels asssociated with the $^2P_{1/2}$ state of the ion.

The ratio of the partial cross sections for xenon behaves in a manner similar to that of krypton. A single peak in R coincides with the resonance that has been associated with one of the Rydberg series members converging to the $5s\,5p^6(^2P_{1/2})$ limit. The peak in R implies that the resonance decays more strongly, but not entirely to the channels associated with the $^2P_{1/2}$ final ionic state. The shoulder on the high-energy side of the curve in xenon, absent in krypton, implies that the weaker resonance at 21.03 eV decays with a slightly higher probability with the continuua associated with the $^2P_{1/2}$ ionic state than with the $^2P_{3/2}$ state. The measurements corroborate the data of Codling *et al.*[28] but are not at all in agreement with the peak value of R equal to 8.8($\pm$0.5) obtained by Kemeny *et al.*[26] from a theoretical extrapolation of their six data points.

The further interpretation of these qualitative remarks for the behavior of β and R in a resonance must await a more complete theoretical interpretation of the lowest two-electron excitation states. In this connection, these results provide new information on the characteristics of these states and how they interact. We hope that these data will stimulate new theoretical initiatives perhaps using the formalism of the relativistic multichannel quantum-defect theory for these rather complex but important systems.

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