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$^2P_{3/2}$:$^2P_{1/2}$ partial photoionization cross-section ratios in the rare gases*

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The $^2P_{3/2}$:$^2P_{1/2}$ partial photoionization cross-section ratios have been measured for the rare gases in the ionization continuum and within resonance structure. The wavelength range for this study was from the $^2P_{1/2}$ ionization threshold to 304 Å. The ratio of the cross sections was found to be constant over this wavelength range, yielding ratios of 1.54, 1.77, 1.93, and 2.18 for Xe, Kr, Ar, and Ne, respectively. Within resonances, the ratio changed dramatically. Results are illustrated for xenon.

INTRODUCTION

Photoionization of the outer p-shell electrons of the rare gases (Ne, Ar, Kr, and Xe) produces ions in two states of excitation caused by spin-orbit coupling. These are the $^2P_{3/2}$ ground state and the $^2P_{1/2}$ excited state of the ion. To obtain the partial photoionization cross sections $\sigma_{3/2}$ and $\sigma_{1/2}$ for producing these states of the ion the technique of photoelectron spectroscopy is used. This involves measuring the ratio R of the number of electrons ejected with energies corresponding to the two states of the ion. The partial cross sections are then given by

$$\sigma_{3/2}=\sigma_p R/(1+R), \quad \sigma_{1/2}=\sigma_p/(1+R), \tag{1}$$

where σ_p is the total photoionization cross section of the outer p-shell electrons. A full description of the method has been given previously.[1]

Several measurements of R have been reported at a few individual wavelengths.[2-4] Two measurements of R have been reported as a function of wavelength.[1,5] However, in all of these measurements no account was taken of the angular distribution of the electrons. Furthermore, all electron energy analyzers used in the past for these measurements were sensitive to any variation in the electron angular distribution. It is now known that the angular distribution of electrons, characterized by the asymmetry parameter β, can vary rapidly with the kinetic energy of the ejected photoelectron. This is especially true for low-energy electrons and within autoionizing resonances.[6-8] Thus, small corrections are necessary for all previously published data, especially for Xe, where the two groups of electrons differ in energy by 1.3 eV.

The ratio $\sigma_{3/2}:\sigma_{1/2}$ has never been measured within an autoionizing resonance. Measurements of R, uncorrected for the angular distribution of the photoelectrons, have been made previously within three window-type resonances in Xe,[1] but because β was unknown, determination of the partial cross sections in the resonances was not possible. Now, however, the availability of both theoretical and experimental values of β over a large range of photoelectron energy,[6,9-15] even though still *not* within the resonances of interest, permit the beginnings of an analysis of the previous measurements within resonances as shown in the following section.

Meanwhile, studies have been initiated on the behavior of β and the $\sigma_{3/2}:\sigma_{1/2}$ ratio within resonances. Theoretical predictions of Dill[7] on the behavior of $\beta_{3/2}$ in the resonance region between the $^2P_{3/2}$ and $^2P_{1/2}$ thresholds in xenon were verified experimentally by Samson and Gardner.[8] These studies show that for the resonances studied, β varies sharply within the resonances as a function of photoelectron energy. Complementary theoretical studies have been done recently by Starce[16,17] on the behavior of the $\sigma_{3/2}:\sigma_{1/2}$ ratio within resonances. Using Fano-type formulas,[18] Starace has given the $\sigma_{3/2}:\sigma_{1/2}$ branching ratio within a resonance as a function of photoelectron energy ϵ. This function is equal to the $\sigma_{3/2}:\sigma_{1/2}$ ratio away from the resonance multiplied by a fraction whose numerator and denominator are quadratic polynomials in ϵ. The coefficients of the polynomial in the numerator depend on properties of the $^2P_{3/2}$ ion state channels and the coefficients of the polynomial in the denominator depend on properties of the $^2P_{1/2}$ ion state channels. The theory predicts that the $\sigma_{3/2}:\sigma_{1/2}$ ratio within a resonance will oscillate once both above and below its off-resonance value as a function of ϵ. Calculations are now under way[17] to calculate the magnitude of the oscillations of the $\sigma_{3/2}:\sigma_{1/2}$ ratio within the $5s5p^6 6p(^1P_1)$ resonance in xenon.

The present investigation has repeated and extended the wavelength range of the previous measurements of R and presents experimental evidence that the ratio of the partial cross sections changes significantly within window-type resonances.

EXPERIMENTAL

Our previous results were obtained with a spherical-grid retarding-potential electron-energy analyzer. The photoelectrons were observed at right angles to the incident photon beam and were collected over an angle of 60°. Under these conditions the number of electrons N_j ejected from a specific state j per incident photon is given by

$$N_j = C\sigma_j[1 + 0.2\beta_j(3P+1)], \tag{2}$$

where P is the degree of polarization of the incident radiation, β_j is the asymmetry parameter defining the angular distribution of the photoelectrons, σ_j is the partial photoionization cross section for the state j, and C is a constant for a given analyzer and gas pressure. From Eq. (2) the ratio of the $^2P_{3/2}:{}^2P_{1/2}$ cross sections is given by

$$\frac{\sigma_{3/2}}{\sigma_{1/2}} = \frac{N_{3/2}}{N_{1/2}} \frac{1+0.2\beta_{1/2}(3P+1)}{1+0.2\beta_{3/2}(3P+1)} . \tag{3}$$

Thus, the ratio R is not simply equal to $N_{3/2}/N_{1/2}$ but must equal the right-hand side of Eq. (3). From Eq. (3) the branching ratios of the previous work can be corrected. The degree of polarization of the radiation, as a function of wavelength, emitted from the monochromator is known.[1] Values of the angular-distribution asymmetry parameter were taken from the calculations of Manson.[6]

New data were taken for each of the rare gases over the extended wavelength region from the $^2P_{1/2}$ threshold to 304 Å. These measurements were made with a cylindrical-mirror electron-energy analyzer designed to accept electrons emitted at 54°44′ to the direction of the incident photon beam.[20] At this angle the number of electrons observed from a given state is independent of P and β.[19,21,22] The energy resolution in both the previous and the present data was about 30 MeV, full width at half-maximum.

The spherical-grid retarding potential analyzer has a much larger transmission than the cylindrical mirror analyzer. Thus, the spherical-grid instrument was capable of operating in an analog mode. This allowed the use of a spark discharge light source that provided a large number of emission lines.[23] With the cylindrical-mirror analyzer electron-counting techniques were necessary and only dc-type light sources could be used. It was thus impossible to probe resonance structure with the cylindrical-mirror analyzer in the present experiment.

RESULTS

Continuum branching ratios

The corrected and new $^2P_{3/2}:{}^2P_{1/2}$ ratios of the rare gases are shown in Fig. 1 as a function of the kinetic energy of the $^2P_{1/2}$ electron. The new data are shown with error bars, which represent the statistical error in the electron-counting procedure. The estimated error in the corrected data is ±8%. The wavelength regions where Rydberg series exist leading to the ejection of s-shell electrons are shown in Fig. 1 by the shaded area above each curve. However, structure in the absorption spectrum continues to shorter wavelengths beyond the s-shell threshold.[24-26] Data points coinciding with known resonances have been omitted from Fig. 1, but one of these will be discussed in detail below.

The ratio of the partial cross sections remains remarkably constant over the entire spectral range. The average values of the ratios are given by the solid line and are listed above each curve. In neon there appears to be a downward trend in the data for the first few points of our previous data. However, before correction these data points had a constant value of 2.18 for the ratio. The corrected values, as shown in Fig. 1, are sensitive to the value of β chosen. We chose the values calculated by Manson.[6] In this case β decreases rapidly from −0.2 to −0.5 for electron energies between 0 and 0.7 eV, then it starts to increase as the electron energy increases. The single data point at 1.4 eV was taken with the cylindrical-mirror analyzer, which is insensitive to any variation in β. The error spread in each of the solid data points and the uncertainty of the theoretical value of β for very-low-energy electrons does not allow any conclusions to be drawn at this time regarding the slight downward trend in the threshold values of Ne.

The statistical branching ratio for each of the rare gases is 2 : 1. Clearly, Kr and Xe lie below this value and Ne slightly above. The constancy of the ratios in the rare gases is in marked contrast to the results in mercury reported by Dehmer and Berkowitz.[27] Walker *et al.*[28] calculated the variation in the $^2D_{5/2}:{}^2D_{3/2}$ branching ratio of Hg and formulated the general rule that the branching ratio is expected to be greater than the statistical value if the photoionization cross section is increasing towards shorter wavelengths and less than the statistical value if the cross section is decreasing. Although this is true for Kr and Xe over the range studied, it is not true for Ne and Ar. Both Ne and Ar have rising cross sections at the $^2P_{1/2}$ threshold and decreasing cross sections in the vicinity of 304 Å,[29] yet the Ne ratio is in excess of the sta-

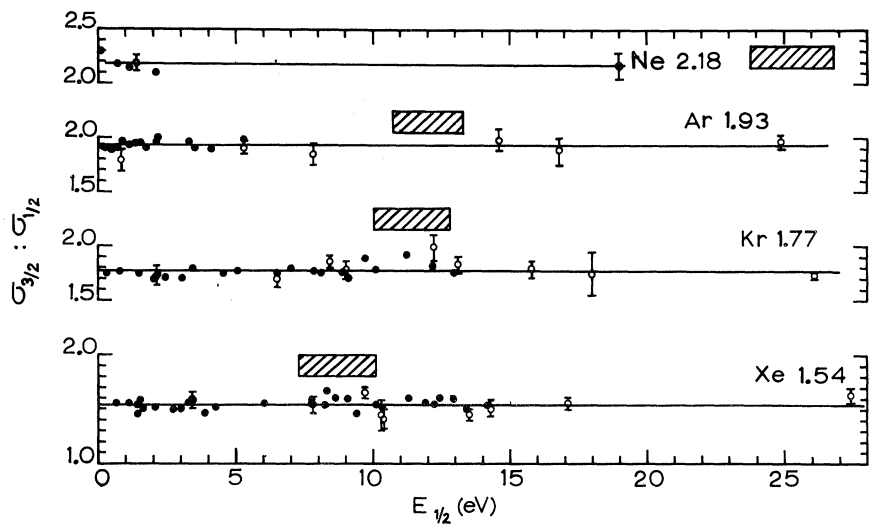

FIG. 1. $\sigma_{3/2}:\sigma_{1/2}$ partial photoionization cross sections of Ne, Ar, Kr, and Xe as a function of the energy of the $^2P_{1/2}$ electron. The shaded area above each curve represents the region of Rydberg states leading to the ejection of s-shell electrons. The solid data points represent the corrected data of Ref. 1. The data points with the error bars represent new data taken with a cylindrical-mirror analyzer.

tistical ratio over the entire wavelength range and Ar is consistently less than 2 : 1. The calculated branching ratios of Xe by Walker and Waber,[30] and by Lu[31] are in excellent agreement with the present results.

Resonance branching ratios

Several discrete light-source emission lines of Ne coincide with window-type resonances in Xe.[1] The most interesting of these in the Ne IV line at 543.891 Å, which coincides with a sharp window-type resonance at 543.89 Å.[24]

The observed ratio of the number of $^2P_{3/2}$ to $^2P_{1/2}$ electrons at this wavelength was 0.77 in contrast to the continuum ratio of 1.54. The identification of the emission line was obtained from the new compilation by Kelly and Palumbo.[32]

The partial cross section within a resonance at a wavelength λ_0 is given by Eq. (2). For example, with $j=\frac{3}{2}$,

$$\sigma_{3/2}(\lambda_0)=C\frac{N_{3/2}(\lambda_0)}{1+0.2\beta_{3/2}(\lambda_0)[3P(\lambda_0)+1]}\ . \tag{4}$$

A similar expression holds outside a resonance with λ_0 being replaced with λ. Thus, when measurements are made in the continuum and within a resonance C can be eliminated and we obtain

$$\sigma_{3/2}(\lambda_0)=\sigma_{3/2}(\lambda)\,\frac{N_{3/2}(\lambda_0)}{N_{3/2}(\lambda)}\,\frac{1+0.2[3P(\lambda)+1]\beta_{3/2}(\lambda)}{1+0.2[3P(\lambda_0)+1]\beta_{3/2}(\lambda_0)}\ . \tag{5}$$

The continuum partial cross sections $\sigma_{3/2}(\lambda)$ were derived from Eq. (1) with $R=1.54$ and σ_p was obtained from previously published data.[29] The relative number of electrons ejected per incident photon $N_{3/2}$ was measured over a small wavelength range about the resonance and within the resonance. The degree of polarization P of the monochromator was measured as a function of wavelength.[1] All the parameters on the right-hand side of Eq. (5) are known except $\beta_{3/2}(\lambda_0)$. A similar expression is obtained for $\sigma_{1/2}(\lambda_0)$. The sum of the partial cross sections must equal the total cross section $\sigma_p(\lambda_0)$, that is,

$$\sigma_p(\lambda_0)=\sigma_{3/2}(\lambda_0)+\sigma_{1/2}(\lambda_0)\ . \tag{6}$$

Thus, an independent measurement of the total cross section within the resonance gives an equation with two unknowns, namely, $\beta_{1/2}(\lambda_0)$ and $\beta_{3/2}(\lambda_0)$. A value of 21.5×10^{-18} cm^2 was obtained for $\sigma_p(\lambda_0)$. When values of $\beta_{1/2}(\lambda_0)$ are selected

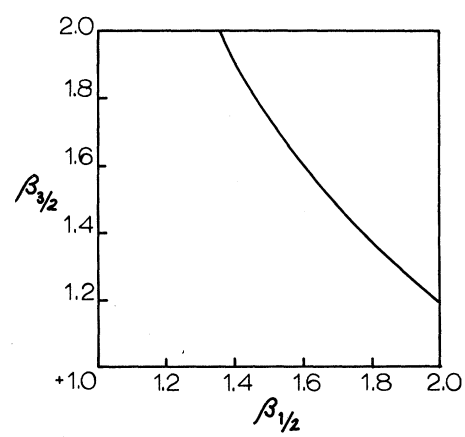

FIG. 2. All possible values of $\beta_{3/2}(\lambda_0)$ and $\beta_{1/2}(\lambda_0)$ that satsify Eqs. (5) and (6) for 544 Å.

TABLE I. Possible values of the partial cross sections of xenon within resonances for the range of β values shown in Fig. 2. The continuum value of the ratio $\sigma_{3/2}:\sigma_{1/2}$ is 1.54. The cross sections are given in units of megabarns (1 Mb $=10^{-18}$ cm^2).

	$\beta_{1/2}(\lambda_0)$									Continuum β values [a]	
	2	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	$\beta_{1/2}(\lambda)$	$\beta_{3/2}(\lambda)$
544 Å $\beta_{3/2}(\lambda_0)$	1.19	1.28	1.37	1.48	1.61	1.75	1.92	···	···	1.60	1.65
$\sigma_{1/2}(\lambda_0)$	10.8	11.1	11.5	11.8	12.2	12.6	13.0	···	···		
$\sigma_{3/2}(\lambda_0)$	10.8	10.4	10.1	9.8	9.4	9.0	8.5	···	···		
$\sigma_{3/2}:\sigma_{1/2}$	1.00	0.94	0.88	0.83	0.77	0.71	0.65	···	···		

[a] These are the β values at the wavelength of the resonance (as obtained from Ref. 6), but in the absence of the resonance.

between the allowed range from +2 to −1 then Eq. (6) can be solved for the corresponding values of $\beta_{3/2}(\lambda_0)$. The ranges of $\beta_{1/2}(\lambda_0)$ and $\beta_{3/2}(\lambda_0)$ were calculated in this way for the 544 Å resonance, and are shown in Fig. 2. These results show, fortunately, that the range of β values satisfying Eq. (6) is not large. For each pair of possible values for the β's, the partial cross section can be calculated using Eqs. (5) and (6). The results are given in Table I. Figure 3 gives the continuum values of the total and partial cross sections. Regardless of the choice of β values the resonance in $\sigma_{3/2}$ is thus predicted to be of the window-type. The actual magnitude of the minimum depends on the correct $\beta(\lambda_0)$ values. However, the perturbation of the $\sigma_{1/2}$ continuum causes an *increase* in the partial cross section regardless of the $\beta(\lambda_0)$ values chosen. Although the effect of the resonance at 544 Å on the partial cross sections is large, it seems to give a very weak window resonance in the total cross section.[24] This resonance shows, unambiguously, that the ratio of the partical cross sections varies dramatically from the continuum value. The fact that this resonance is so weak in the total cross section but strong in the partial cross sections leads to the speculation that some resonances may not be observable by absorption spectroscopy, but may show up only in photoelectron spectroscopy. For example, the Kr ratio at 460.728 Å is much higher than the surrounding values. However, no observable resonance occurs in the total absorption spectrum.[24]

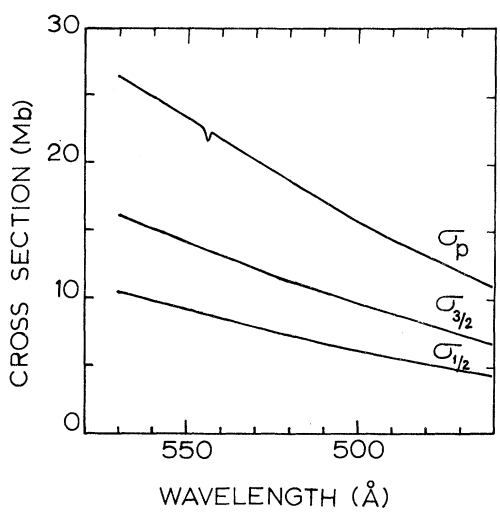

FIG. 3. Continuum values of the total and partial cross sections for the wavelength region 460–570 Å (1Mb $=10^{-18}$ cm^2). Many resonances exist in this wavelength region, however, the only resonance shown is the window resonance at 544 Å in the total cross section curve with $\sigma_p(544\ \text{Å}) = 21.5\times10^{-18}$ cm^2.

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