Angular Distributions of *s*-Subshell Electrons in Open-Shell Atoms: 3*s* Photoionization of Atomic Chlorine

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A determination of the angular distribution parameter β of the atomic chlorine $3s$ photoelectrons over the photon-energy range from 29 to 70 eV has been carried out using electron spectrometry in conjunction with synchrotron radiation. Our results confirm the basic theoretical predictions that β, for s-subshell photoionization in open-shell atoms, is in general term and photon-energy dependent, in contrast to closed-shell atoms where β is always 2 nonrelativistically. However, our measurements of β for the Cl$^+$ $3s(^{1,3}P)$ channels demonstrate that significant details are not handled well by simple Hartree-Fock theory.

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The angular distribution of photoelectrons in general varies as a function of photon energy due to the interference of the two possible partial waves that result from the photoionization process in the dipole approximation, i.e., $\varepsilon_{\ell+1}$ and $\varepsilon_{\ell-1}$. Here ε represents the kinetic energy of the photoelectron and ℓ is the angular momentum quantum number of the atomic subshell being photoionized. An exception to this general behavior is the photoionization of s-subshell electrons in closed-shell atoms in the absence of relativistic effects. In this case $\ell = 0$ and only *one* partial wave is allowed, with an angular momentum quantum number of 1, i.e., a p wave. This leads to an angular distribution parameter, $\beta = 2$, *independent* of the energy of the ionizing radiation [1] ($\beta = 2$ corresponds to emission of the photoelectron primarily along the electric-field vector of the ionizing radiation).

In the case of s-subshell ionization of most open-shell atoms, however, this result no longer holds although there is only *one* outgoing partial wave. In open-shell atoms there is generally more than one ionization channel available. Assuming that LS coupling is valid, the ground state term of an open-shell atom is ^{2S+1}L, where L is generally not zero as in the case of closed-shell atoms [2]. In the dipole approximation the selection rules governing the photoionization of an open-shell atom require that $^{2S+1}L \rightarrow {}^{2S+1}(L-1)$, ^{2S+1}L, $^{2S+1}(L+1)$. Interference between these various ionization channels is likely, leading to (i) $\beta \neq 2$, (ii) term dependent β values, and (iii) photon-energy dependent β values. This cannot occur in a closed-shell atom because the ground state term is a ^1S, which can only proceed to a *single* final-state channel, a ^1P. Hence, there is no possibility for interference. It must be mentioned, however, that, in the relativistic case, β for s-subshell photoionization in closed-shell atoms is in general photon-energy dependent. This is because relativistically there are *always* two possible partial waves, $\varepsilon p_{1/2}$ and $\varepsilon p_{3/2}$. These waves can interfere and thereby lead to a photon-energy dependent β value. A classic example of this is $5s$ photoionization of Xe [3].

While theoretical predictions of the term and photon-energy dependence of β for $3s$-subshell photoionization of atomic chlorine were first made more than 20 years ago [4], and later for other asymmetric open-shell atoms ($L > 0$) [5], there has been no experimental confirmation of these predictions to date. This is due in part to the difficulty of producing a good atomic beam of open-shell atoms, especially for atomic chlorine, in conjunction with the rather weak cross sections of s-subshell electrons, making it difficult to obtain good statistics. In this Letter we present an experimental examination of these predictions for the representative case of $3s$ photoionization of atomic chlorine.

The experiment was carried out on the PGM-undulator beam line [6] at the Aladdin storage ring in Stoughton, Wisconsin. The experimental setup utilizes a microwave discharge tube to dissociate a suitable molecule, such as Cl$_2$, into its constituent atoms. In addition, Ar and Ne were occasionally added to help stabilize the discharge and also to provide built-in calibration lines. Based on previous measurements under similar conditions [7], we do not expect the population of excited states in the discharge to be greater than 5%. A more detailed description of the discharge setup can be found in Refs. [8,9]. The electron spectrometer [10] contains three electrostatic analyzers mounted at right angles to each other on a rotatable platform which lies in a plane perpendicular to the incoming photon beam. In the dipole approximation, the electron intensity $I_i(\theta)$ of the photoelectrons ejected at an angle θ with respect to the polarization vector of the synchrotron radiation is given by

$$I_i(\theta) \propto \frac{d\sigma_i}{d\Omega} = \frac{\sigma_i}{4\pi}\left(1 + \frac{\beta_i}{4}(1 + 3p\cos 2\theta)\right). \quad (1)$$

Here $d\sigma_i/d\Omega$ is the partial differential cross section for the emission of an electron from the subshell i, σ_i is the partial cross section, β_i is the angular distribution parameter, and p is the degree of linear polarization of the photon beam. By simultaneously measuring both $I_{3s}(0°)$ and $I_{3s}(90°)$ and forming the ratio $R = I_{3s}(0°)/I_{3s}(90°)$, β can be found from

$$\beta = \frac{4(R - 1)}{3p(R + 1) - (R - 1)}, \qquad (2)$$

where the degree of linear polarization, p, was determined to be 0.985(5) in a separate set of calibration measurements. In addition, the ratio R of the measured intensities was corrected for possible differences in the source volume as seen by the analyzers at 0° and 90° as well as for differences in the detection efficiency of the two analyzers. The needed correction factors were obtained from β measurements of suitable rare-gas photoelectrons. To protect the integrity of the monochromator from the reactive target gases, the interaction region was separated from the monochromator exit mirror by a 100 nm Al filter. For the purposes of this experiment, no stringent calibration of the photon energy was required, and all stated photon energies are accurate to better than 0.05 eV. The nominal photon energy bandpass was about 30 meV at a photon energy of 50.0 eV.

In the present experiment, the basic reaction is

$$[\mathrm{Ne}]3s^2 3p^5(^2P) + h\nu \rightarrow [\mathrm{Ne}]3s3p^5(^{1,3}P) \times \varepsilon p(^2S, ^2P, ^2D),$$

where [Ne] represents the inner-shell electrons not involved in the photoionization process. Because the photoion can have two different terms and still satisfy the dipole selection rules, there will be two distinct $3s$ photoelectrons with different binding energies, the $3s(^3P)$ and the $3s(^1P)$. An example of a typical chlorine photoelectron spectrum is shown in Fig. 1. This figure also illustrates the basic procedure used in obtaining a pure atomic chlorine photoelectron spectrum (PES). The upper panel shows a PES spectrum recorded at $h\nu = 50$ eV with the discharge on. Because the discharge does not produce 100% dissociation, the spectrum is a mixture of atomic chlorine and the residual undissociated precursor molecule. The middle panel is a discharge-off spectrum of Cl_2 only. After subtracting the underlying background from each spectrum, the discharge-off spectrum is then normalized to an isolated molecular peak in the discharge-on spectrum (in this instance the molecular peak near 26.5 eV was used) and subtracted from it. The subtracted result, containing atomic chlorine and the argon additive, is shown in the bottom panel. Clearly visible are the two $3s$ photoelectron lines, the $3s(^3P)$ and the $3s(^1P)$, with binding energies of 24.54(4) and 27.30(4) eV, respectively, in excellent agreement with our earlier results [8]. Extraction of the $3s(^1P)$ photoelectron peak from the data frequently proved difficult because it sits virtually atop a molecular photoelectron line. The integrated areas of the resulting peaks were then extracted at both 0° and 90° and used to form R from which β could then be found from Eq. (2).

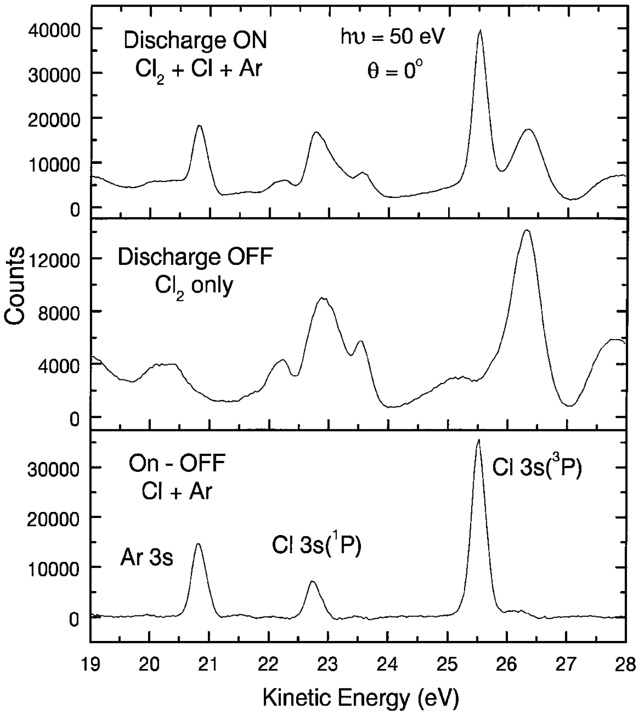

FIG. 1. Discharge-on photoelectron spectrum of Cl + Cl_2 + Ar (upper panel). The step size is 40 meV. Discharge-off photoelectron spectrum of Cl_2 only (middle panel). The Cl $3s$-photoelectron spectrum (lower panel) resulting from the subtraction of the middle panel from the upper panel. See text for details.

Our experimental β values for both the $3s(^3P)$ and the $3s(^1P)$ photoelectrons as a function of photon energy are displayed in Fig. 2 and reported in Table I. Both plots show a clear and unambiguous dependence of β on the term of Cl^+ and on the photon energy of the ionizing radiation, in qualitative agreement with theory for the open-shell case [4,5]. In the upper panel the dotted line corresponding to $\beta = 2$ is to remind the reader of the result for closed-shell atoms in the absence of relativistic effects.

For both the $3s(^3P)$ and, in particular, the $3s(^1P)$, several points deviate markedly from a smooth curve. These points are indicated by the open circles. We believe that this deviation is likely due to the presence of doubly excited states of the type $3s^2 3p^3 n\ell m\ell'$ at photon energies of 30 and 38 eV which then autoionize into the same final-state channels as produced by direct $3s$ photoionization. This interpretation is reinforced by the appearance of a strong satellite line with a binding energy about 0.38(3) eV lower than the $3s(^1P)$ photoelectron line. This satellite appears only in the spectra recorded at 30 and 38 eV. Since it only appears at these energies, we conclude that it arises from the decay of a $3s^2 3p^3 n\ell m\ell'$ excited state.

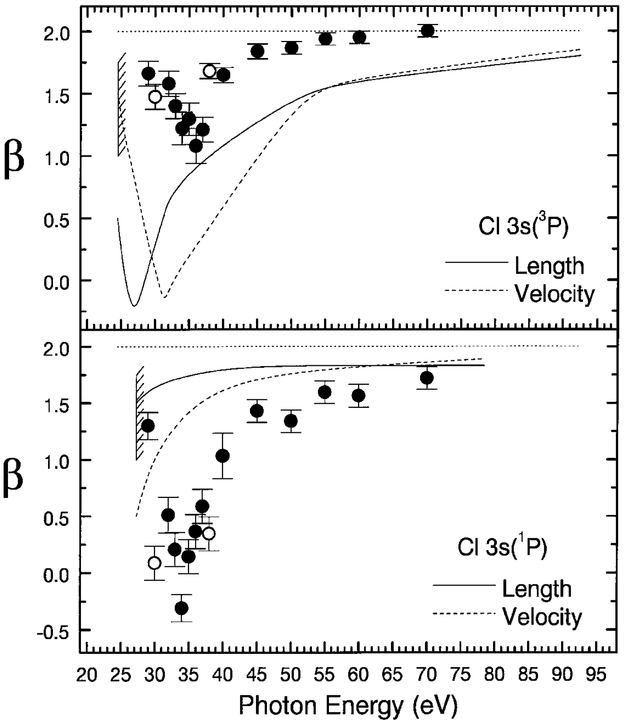

FIG. 2. Experimental and theoretical β values for the $3s(^3P)$ (upper panel) and the $3s(^1P)$ (lower panel) photoelectron lines. Circles are the experimental values. The open circles correspond to photon energies where suspected doubly excited neutral excitations are present. The solid lines correspond to calculations [4] in the length gauge, and the dashed lines in the velocity gauge. The dotted line at $\beta = 2$ is the result for closed-shell atoms in the absence of relativistic effects. The $3s(^{3,1}P)$ ionization thresholds [8] are also indicated.

Also shown in Fig. 2 are the length and velocity gauge calculations from Ref. [4]. The calculations were done using Hartree-Fock continuum orbitals calculated in the field of a relaxed ion core. The bound state wave functions were obtained in part from the Hartree-Fock code of Froese-Fischer [11]. The calculations are entirely nonrelativistic and no account of electron correlation beyond the Hartree-Fock model was considered (e.g., configuration interaction). While qualitative agreement between theory and experiment is good for the $3s(^3P)$ case, theory significantly overestimates the magnitude of the dip in β as well as the location of the minimum. Furthermore, the data indicate a more rapid approach towards $\beta = 2$ than predicted by theory. In the case of the $3s(^1P)\beta$ parameter, there is a major discrepancy between experiment and theory. Theory predicts that the minimum occurs below the $3s(^1P)$ ionization threshold, while experiment shows a clear minimum above the ionization threshold within the continuum. The disagreement between theory and experiment is not too surprising considering the level of approximations used in these pioneering calculations. For example, the difference in the results for the two gauges gives a clear indication of the quality of the wave functions. If the wave functions were exact solutions of the Schrödinger equation, then there would be no difference in the length and velocity gauge results.

Discrepancies between the single particle Hartree-Fock results and experiment may be attributed to the presence of strong interchannel interactions and configuration interaction, including ionization with excitation (shake satellites) in analogy to the case of Xe 5s photoionization [3]. Inclusion of these interactions would have two effects: (i) the depth of the minimum would be lessened, and (ii) the position of the minimum would be shifted. Both effects can be seen in the data where effect (i) is apparently stronger for the $3s(^3P)$ term. In addition, shifts of the minima of β for both terms are significant, where the shift of the $3s(^1P)$ minimum is sufficiently large to move it from the region of discrete excitations into the continuum. While no 3s correlation satellites are plainly evident in the spectrum of Fig. 1 recorded at $h\nu = 50$ eV, they are clearly discernible in our spectra recorded at lower photon energies (e.g., $h\nu = 32$ eV), indicating that satellite processes are indeed relevant to 3s photoionization of atomic chlorine.

According to theory, the minima of the theoretical β curves for the $3s(^3P)$ photoelectron peak occur in the region of a Cooper minimum [12]. In this photon-energy region, the radial dipole matrix element corresponding to the $3s3p^5(^3P)\varepsilon p(^2D)$ final-state channel is zero. While the other two matrix elements, those corresponding to the ^2S

TABLE I. Angular distributions of the atomic chlorine $3s(^3P)$ and $3s(^1P)$ photoelectrons.

	β			β	
$h\nu$ (eV)	$3s(^3P)$	$3s(^1P)$	$h\nu$ (eV)	$3s(^3P)$	$3s(^1P)$
29	1.66(10)	1.30(12)	38[a]	1.68(6)	0.35(15)
30[a]	1.47(10)	0.09(15)	40	1.65(6)	1.03(20)
32	1.58(10)	0.51(16)	45	1.84(6)	1.43(10)
33	1.40(10)	0.21(15)	50	1.86(6)	1.34(10)
34	1.22(13)	−0.31(12)	55	1.94(5)	1.60(10)
35	1.30(13)	0.14(15)	60	1.95(5)	1.56(10)
36	1.08(14)	0.36(15)	70	2.00(5)	1.72(10)
37	1.21(10)	0.59(15)	···	···	···

[a] These photon energies likely correspond to resonance excitations.

and the ^2P, are not zero (in particular, the ^2S), the variation of β can be expected to be significant in a photon-energy region where one of the dipole matrix elements is zero. Our experimental results qualitatively support this picture. Although we have not yet systematically extracted the relative partial cross sections of the $3s(^3P)$ and the $3s(^1P)$ photoelectron peaks from our data, they clearly indicate a minimum in both *partial cross sections* in the vicinity of the experimental β curve minima. This indicates that the β curve minima occur in a photon-energy region close to a Cooper minimum.

In conclusion, we have presented the first experimental confirmation of the term and photon-energy dependence of β of the $3s$-subshell electrons in the open-shell chlorine atom arising solely from nonrelativistic effects. These results should hold equally true for other asymmetric open-shell atoms, in accordance with earlier qualitative theoretical considerations [5]. We have established the magnitude and character of the β parameter for both $3s$ photoelectrons through and beyond the "open-shell induced" $3s$ Cooper minimum. The discrepancy between theory and experiment is thought to be primarily due to the neglect of important interchannel and configuration interactions in the calculation. While future calculations will be even more complex than those made for $5s$ photoionization in the closed-shell xenon atom, they will be highly desirable to gain a clear understanding of the dynamic processes in open-shell atoms.

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[2] For open-shell atoms with half-filled subshells, $L = 0$ in the ground state, and β of s-subshell photoelectrons will again be 2 in the absence of relativistic effects. This would include all alkali atoms, and a few other atoms such as Mn (^6S) and Eu (^8S).

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