

## Population of the ${}^3P_{2,1,0}$ fine-structure states in the $3s$ and $3p$ photoionization of atomic chlorine

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In a high-resolution photoelectron-spectrometry study of the photoionization of chlorine atoms in both the  $3s$  and  $3p$  subshells, we were able to resolve contributions from ionic states with specific  $J$  values and measure the relative populations of these fine-structure components. Our photoelectron spectra, recorded at  $h\nu = 29.2$  eV, give ratios of  ${}^3P_2 : {}^3P_1 : {}^3P_0 = 100:40.5:9.5$  for  $3p$  photoionization and  ${}^3P_2 : {}^3P_1 = 100:31$  for  $3s$  photoionization. While the results for  $3p$  ionization are in accord with predictions based on a simple geometric analysis, the contribution of the  ${}^3P_1$  state in  $3s$  photoionization is larger than that predicted by this simple model. The geometric predictions are also compared with results from a similar measurement of the population of the  $4p^{-1}({}^3P_J)$  states produced in the  $4p$  ionization of Br and with earlier work on the production of  ${}^3D_{2,1,0}$  states in  $d$ -shell photoionization of Cu and Ag.

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Because of the relative ease of handling atoms with a closed-shell structure in the ground state, electron-spectrometry studies in atomic physics employing synchrotron radiation have concentrated heavily on such systems. In addition, the simplicity introduced into calculations by having all angular momenta for the initial state equal to zero have meant that detailed theoretical analyses have also focused on closed-shell atoms. The result has been a considerable advance in the understanding of the influence of correlation on electron dynamics and a rather comprehensive description of the ionization of closed-shell systems. To date this understanding has not been matched in the analysis of open-shell atoms, particularly those having nonzero orbital angular momentum in the partially filled shell.

One source of evidence for the influence of electron correlations on photoionization dynamics in closed-shell atoms was the deviation of the branching ratios into the various fine-structure components from the statistical values expected for closed-shell systems based on geometric considerations [1]. One might be inclined to use similar arguments in the case of open-shell atoms, in which the deviations from the simplest single-particle descriptions serve as signatures for the effects of dynamical couplings. However, in the case of the latter, the interpretation of the experimental results is complicated by the necessity of ascertaining the influence of the angular-momentum coupling on the behavior of the branching ratios. Theoretical analyses [1-5] have shown that, for open-shell atoms, the analogy to the statistical branching ratio obtained for the closed-shell system in the ab-

sence of electron correlation is the more general geometric branching ratio. For the case under consideration in this work, in which the direction and the final-state quantum numbers of the photoelectron are not observed, this ratio depends only on the values of the angular momenta in the initial and final ionic states. It reduces to the  $2J_c + 1$  statistical result in the limit in which all the initial angular momenta are equal to zero.

Although there have been a number of experiments on the halogen atoms, prototype open-shell systems with nonzero orbital angular momentum, these have concentrated primarily on total absorption, or an equivalent quantity [6], in which a differentiation into the final ionic states is not possible. Photoemission measurements which can distinguish fine-structure components in the ionic state do exist [4, 7-11], but these were generally recorded at one energy only and at an emission angle at which the effects of the anisotropic angular distribution on the measurement can distort the results for the relative populations. Recently more efforts have been directed toward emission experiments in which partial cross sections are obtained directly, independent of angular-distribution effects, and at variable photon energy [11]. This work has been facilitated by the ever-improving performance of monochromators which provide the resolution which is necessary for isolation of the multiplet structure of the more complex open-shell atoms as well as the upgrade of electron storage rings themselves to provide the higher photon fluxes necessary for experiments in emission. As data can now be obtained from these more definitive measurements, it is becoming possible to

test calculations for open-shell atoms at the same level as for closed-shell atoms.

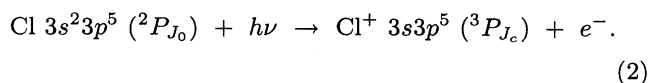
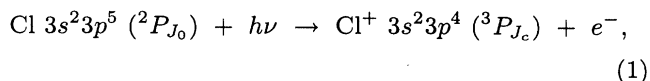
We have recently begun an analysis of the photoionization of the chlorine atom through the use of electron spectrometry with synchrotron radiation [12, 13]. In another article [13] we presented an extensive study of the autoionizing resonances involving the transitions  $3s \rightarrow np, n \geq 4$ . In the present paper we focus on the results of a set of high-resolution measurements targeted toward an analysis of the relative populations of the fine-structure components,  $\text{Cl}^+(^3P_2)$ ,  $\text{Cl}^+(^3P_1)$ , and  $\text{Cl}^+(^3P_0)$ , created in the removal of either a  $3s$  or a  $3p$  electron. We will compare our experimental data with predictions based on the geometric ratios and with concomitant calculations which include the effects of an  $LS$ -dependent dynamical matrix element made by Pan and Starace [5] for both  $3s$  and  $3p$  ionization. The comparison will include data from an analysis of the detailed spectra we reported recently for the  $4p$  subshell of the bromine atom [11]. To extend the comparison between theory and experiment, and to place the study in a broader perspective, we also summarize the most relevant results from earlier measurements made on ionization of Cu and Ag [14–18].

The details of the experiments on atomic chlorine have been outlined in previous publications [12, 18]. However, it is appropriate that we review several points which will have bearing on our results. The chlorine atoms are produced in a microwave discharge tube from the dissociation of  $\text{Cl}_2$  gas in a buffer of argon. The interior of the tube is coated with  $\text{P}_2\text{O}_5$  to suppress recombination on the walls. The discharge is connected with the source region of the electron spectrometer via a 30-cm-long tube which is itself coated with a halocarbon wax, also to prevent recombination. The discharge is excited with a 2450-MHz microwave generator powering an Evenson-like cavity. Under typical operation, approximately 70 W of power are fed into the discharge, with 1 to 3 W reflected. The cavity and discharge tube are cooled with a steady flow of compressed air, and the pressure in the tube is held at about 100 mTorr.

All experiments were conducted at the University of Wisconsin Synchrotron Radiation Center. The photons were dispersed by a 6-m toroidal-grating monochromator providing a band pass of about 32 meV at the  $h\nu = 29.2$  eV used in this experiment. We chose this energy so as to be removed from any known resonance structure and from the influence of the  $3p$  Cooper minimum near 42 eV. As an additional precaution against an unexpected interference, a set of high-resolution data was also recorded at  $h\nu = 30.2$  eV. Photoelectrons were retarded before entering the energy analyzer, which was set for a resolution of 30 meV. A PES (photoelectron spectrum) resolution of 55–60 meV was achieved, reflecting the contributions from the band pass of the photon beam, the resolution of the analyzer, and the drift of the surface potentials caused by the reactivity of the chlorine atoms. As seen below, this PES resolution was sufficient to resolve the  $^3P_2$  and  $^3P_1$  components in both cases, to allow for the extraction of the  $^3P_0$  component by a fitting procedure, and to separate the  $\text{Cl}^+$  multiplet lines from the ma-

ior band of the HCl contaminant. At least four spectra were recorded over the  $^3P$  regions of  $3s$  and  $3p$  ionization. Two analyzers were used simultaneously and set to the so-called “magic angle,” at which the differential cross section  $d\sigma_i/d\Omega$  is proportional to the partial cross section  $\sigma_i$  for each  $J$  component  $i$ .

In the discussion which follows we will focus on that portion of the photoelectron spectrum detailing the production of the  $^3P_J$  final ionic states. This is given in Fig. 1, where the right panel shows the spectrum resulting from  $3p$  photoionization, and the left panel shows the spectrum resulting from  $3s$  photoionization. In particular, we will follow the reactions:



In general,  $J_0$ , the initial angular momentum, has the possible values  $J_0 = 3/2$  and  $1/2$ , and  $J_c$ , the final angular momentum, has values  $J_c = 0, 1, 2$ . It follows from the independent electron model and from angular momentum conservation that  $J_0 = J_c + \ell_0 + 1/2$ , where  $\ell_0$  is the orbital angular momentum of the electron being removed. When  $\ell_0 = 0$ , as for  $3s$  ionization, then the values of  $J_0$  and  $J_c$  must satisfy the triangle equality

$$|J_0 - 1/2| \leq J_c \leq |J_0 + 1/2| \quad (3)$$

as long as the dynamical amplitudes do not depend on the values of the initial and final orbital angular momenta  $L$  and  $L'$ . In a more general treatment Pan and Starace [5] have shown that this selection rule no longer strictly holds when the dependence of the dynamical amplitudes on the values of  $L$  and  $L'$  is included, although in numerical calculations the rule appears to be obeyed well.

The fine-structure splitting between the  $^2P_{3/2}$  and

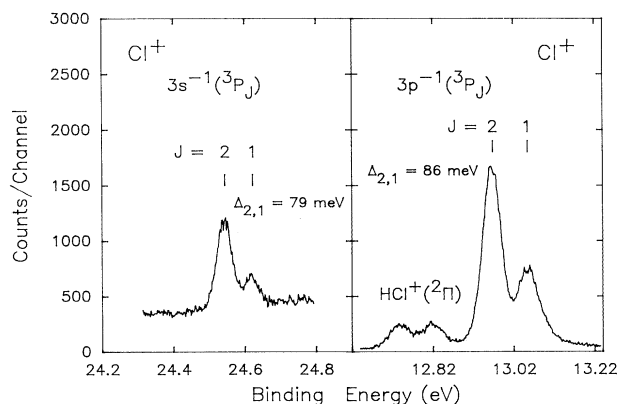


FIG. 1. Photoelectron spectra of  $3s$  and  $3p$  subshells of atomic chlorine showing the  $^3P_{2,1,0}$  fine-structure components. Both spectra were recorded at an angle of  $56^\circ$  with respect to the polarization of the photons with  $h\nu = 29.2$  eV.

$^2P_{1/2}$  states of chlorine is equal to 109 meV. Under the conditions of the discharge there will be a preferential population of the lowest fine-structure component,  $J_0 = 3/2$ . If the dissociation is caused primarily by collisions between the larger atomic and molecular species, then the population in the excited component,  $J_0 = 1/2$ , will be determined by the energy of these species in the discharge. This is on the order of a few kT, with  $T = 300$  K. At these energies the equilibrium population of the excited component would be on the order of a few percent, namely, 0.7%, 5.7%, and 10.9% for  $T = 300, 600,$  and  $900$  K, respectively.

A good indication of the contribution of the excited component to the ionization can be obtained from Fig. 2. The principal features of this spectrum are the  $^3P_2$  and  $^3P_1$  fine-structure components which appear as a consequence of the ionization from the  $^2P_{3/2}$  ground state of the atom. The corresponding contributions arising from the  $^2P_{1/2}$  excited state would appear at the locations designated as  $^3P'_2$  and  $^3P'_1$ . Unfortunately, the presence of the HCl contaminant makes it difficult to determine this contribution with a high accuracy. Nonetheless, through a fitting procedure we derive a small contribution from ionization from the  $^2P_{1/2}$  state into the  $^3P'_2$  ionic state. From the observed ratio of 2.5(1.1)% for the  $^3P'_2$  and  $^3P_2$  lines we estimate an excited-state population of about 7% using the calculated probabilities [5] of 25 for  $^2P_{1/2} \rightarrow ^3P'_1$ , and 10 for  $^2P_{1/2} \rightarrow ^3P'_2$ . A value of 7% seems quite reasonable, indicating a temperature of around 600 K for the heavier species in the discharge. It should be pointed out that using the geometric values for the branching ratios from the  $J = 1/2$  ground state, any contribution to the ionization from the excited state, when subtracted, will cause the  $^3P_2$  branching ratio extracted from the 3s and 3p spectra to decrease slightly.

Up to the level of a few percent, we can then be assured that the ionization is occurring from the fine-structure component having the lowest energy,  $^2P_{3/2}$ . In Table I are given the fully corrected results of the relative populations of the final ionic states at a photon energy of 29.2 eV. In the case of 3s ionization of chlorine, the spectrum could be fit with Pearson-7 functions [19] for two peaks of equal width at the positions of the  $J = 2$  and  $J = 1$  components, leaving no or negligible strength to the  $J = 0$  component. In the case of 3p ionization, the  $\text{HCl}^+(^2\Pi, v = 1)$  doublet occurring near the  $\text{Cl}^+(^3P_0)$

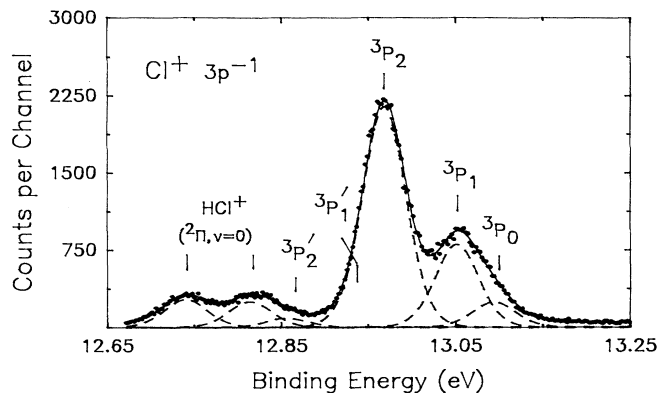


FIG. 2. Chlorine  $3p^{-1}(^3P_J)$  photoelectron spectrum with separation of  $J$  contributions. Points, data after subtraction of background and  $(^2\Pi, v = 1)$  component of  $\text{HCl}^+$ ; solid line, overall fit; dashed lines, individual components. All peaks are given equal widths and are Voigt profiles with a dominant Gaussian component, approximated by an analytic Pearson-7 function. The locations of the final  $^3P_2, ^3P_1,$  and  $^3P_0$  states formed by the ionization of the  $^2P_{3/2}$  ground state are indicated. Also shown are the locations of the corresponding  $^3P'_{2,1}$  states formed by ionization from the  $^2P_{1/2}$  initial excited state.

line and amounting to about 8% of the  $\text{HCl}^+(^2\Pi, v = 0)$  doublet [9] was subtracted from the observed spectrum before fitting. The resulting fit, which yielded the various lines in positions close to expectation, is shown in Fig. 2, with all lines set to have equal widths corresponding to the PES resolution. The peaks are essentially Gaussian, but small tails in the photon profile are accounted for by the inclusion of a small Lorentzian fraction. Values given in Table I are the peak areas given by the fits and are averaged from two spectra each. For  $\text{Cl}^+(3p^{-1})$ , a small contribution of  $^3P'_1$  was subtracted from  $^3P_2$ . Uncertainties are based on the scatter of the data, the accuracy of the fit, and estimated errors occurring in accounting for the  $\text{HCl}^+$  and  $\text{Cl}^+(^3P'_1)$  contributions.

Also included in Table I are results from fits of  $\text{Br}^+(^3P_{2,1,0})$  spectra obtained at the magic angle and  $h\nu = 21.0$  eV in our earlier study of that element [11]. The bromine spectrum arises solely from the  $^2P_{3/2}$  ground state owing to the large excitation energy of 0.46 eV

TABLE I. Fine-structure populations in atomic chlorine and bromine.

Source	$h\nu$ (eV)	$\text{Cl}^+ 3p^{-1}$			$\text{Cl}^+ 3s^{-1}$		$\text{Br}^+ 4p^{-1}$		
		$^3P_2$	$^3P_1$	$^3P_0$	$^3P_2$	$^3P_1$	$^3P_2$	$^3P_1$	$^3P_0$
This work <sup>a</sup>	29.2	100	40.5(1.5)	9.5(2.2)	100	31(3)	100	36(2)	11(2)
Kimura <sup>b</sup>	21.2	100	44(5)	~6			100	51(5)	~6
Van der Meer <sup>c</sup>	21.2	100	40	8.5			100	44	6
Theory <sup>d</sup>		100	36	8	100	20	100	36	8

<sup>a</sup>Br data from fitted spectra ( $h\nu = 21.0$  eV) to data of Ref. [11].

<sup>b</sup>HeI data from Ref. [7], at  $90^\circ$ .

<sup>c</sup>Cl data from our graphical analysis of Fig. 1 of Ref. [9], HeI at  $90^\circ$ ; Br data from Fig. 1 of Ref. [10], HeI at  $90^\circ$ .

<sup>d</sup>Geometric ratios (Refs. [3] and [5]).

needed to reach the  ${}^2P_{1/2}$  state. Good resolution of the  ${}^3P_J$  multiplet was achieved previously in photoelectron spectra recorded at  $90^\circ$  with respect to the unpolarized He I radiation (21.22 eV) for both Cl [7, 9] and Br [7, 8, 10] atoms. However, fine-structure populations were not always given in these studies. As a consequence, some values listed in Table I for the He I work are based on our graphical analysis of these authors' published spectra [9, 10]. The errors due to this secondary treatment of the spectra and a possible bias attendant on differences in angular distribution are probably within several percentage points for Cl, but doubtless greater for Br because of the presence of several autoionization resonances [11] close to the He I energy.

Finally, in Table I are given the theoretical ratios for the removal of an outer  $p$  electron in Cl and Br [3, 5] and the  $3s$  electron in Cl [5]. All the ratios given are purely geometric. The accord between our data and theory is satisfactory for  $\text{Cl}^+ 3p^{-1}$  and good for  $\text{Br}^+ 4p^{-1}$ , but poor for the  ${}^3P_2: {}^3P_1$  ratio for ionization in the Cl  $3s$  subshell. This ratio, 100:31(3), obtained at  $h\nu=29.2$  eV, was essentially unchanged at  $h\nu=30.2$  eV, where values of 100:29(4) were obtained. It appears that the populations of the  ${}^3P_J$  states are dominated by purely geometric effects for the outermost  $p$  subshell. However, the possible increase of the  ${}^3P_0$  population from Cl to Br, which seems to continue when proceeding to I [2], suggests increasing mixing of  ${}^3P_0$  with  ${}^1S_0$ , as already pointed out in Ref. [2]. A mixing of  ${}^3P_2$  with  ${}^1D_2$  would affect all ratios as they are presented in Table I, but the degree of this interaction remains to be determined by an analysis of the relevant cross-section measurements made through the halogen series over an extended energy range. By contrast, in the related case of photodetachment, the populations from  $\text{O}^-$  and  $\text{S}^-$  were found to be geometric [20].

The experimental  ${}^3P_1: {}^3P_2$  ratio for the  $3s$  subshell of Cl is markedly greater than that given by geometric considerations. This might be attributed to mixing of the  $3s^{-1}({}^3P_1)$  state with the  $3s^{-1}({}^1P_1)$  state and to interchannel coupling between the weak  $3s^{-1}, \epsilon\ell$  and the strong  $3p^{-1}, \epsilon\ell$  channels, including the  $3s3p^5({}^3P) \leftrightarrow 3s^23p^3nd, \epsilon d({}^3P)$  interaction. However, a measured value of  $d\sigma/d\Omega(0^\circ) = 3.8(8)$  for the  ${}^3P_{2,1,0}: {}^1P_1$  ratio [13], as

compared with 3.0 for the geometric ratio, lends support to the presence of final-ionic-state mixing in a provisional manner only because of a large uncertainty in the measured ratio and a possible angular dependence. In addition, according to Pan and Starace [5], the inclusion of channel and configuration mixing increases the theoretical ratio by only a small fraction, namely to 100:23. The population of  $3s^{-1}({}^3P_0)$  is zero in the term-independent approximation for the partial cross sections  $\sigma(J_0, J_c)$ . Experimentally, we could not discern a  ${}^3P_0$  contribution in the observed spectrum (see Fig. 1, left panel).

It is instructive to extend the critical comparison made here for the  $np$  and  $ns$  electrons of the halogen atoms to another class of open-shell atoms, the  $(n-1)d^{10}ns$  elements. For these atoms the geometric ratios reduce to the statistical ratios because the ground state is a  ${}^2S_{1/2}$  state. The earliest data [15] obtained for photoionization in the closed  $4d$  subshell of Ag by He II radiation (40.81 eV) were seen to be in good accord with the geometric ratio [3], although the data were recorded at an angle of  $90^\circ$ . Since that time, true cross-section ratios have been obtained for both Ag [17, 18] and Cu [16] as measured at the magic angle ( $54.7^\circ$ ). We summarize these later data in Table II. As can be seen, in the case of Ag, the observation agrees poorly at 21.22 eV with the theoretical prediction but satisfactorily at other energies between 20 and 41 eV for which data exist [18]. The discrepancy occurring at 21.22 eV might be attributed to the presence of a nearby autoionization resonance which could affect the populations, as was indeed observed [17] near 16.7 eV where two-electron excitation states are known to exist [21]. Similarly, the variance between geometric and observed ratios in the case of Cu might be due to interfering excitation states, supported by the fact that the populations of the  ${}^3D_1$  and  ${}^1D_2$  states differ considerably at emission angles of  $90^\circ$  and  $54^\circ$  [14, 16]. The results presented in this paragraph show that the geometric ratios apply also to the fine-structure components created in  $d$ -shell ionization, provided correlation effects are negligible. However, if many-electron interactions are possible, as in the case of autoionization occurring in Ag at 16.7 eV and perhaps in Ag and Cu at 21.2 eV, or in the case of final-state interactions occurring in Rb [15] at

TABLE II. Spin-orbit populations from ionization of a closed  $d$  shell in an open-shell atom.

Element	${}^3D_2$	${}^3D_1$	${}^3D_0$	${}^1D_2$
$(n-1)d^{10}ns^a$	100	71.4	42.9	71.4
Ag <sup>b</sup>	100	77.2(1.4)	43.2(1.2)	79.4(1.4)
Ag <sup>c</sup>	100	72(2)	45(2)	70(3)
Ag <sup>d</sup>	100	70	42	67
Ag <sup>e</sup>	100	67(4)	41(4)	75(5)
Cu <sup>f</sup>	100	90(8)	44(5)	94(8)

<sup>a</sup>Geometric ratios, Ref. [3].

<sup>b</sup>Reference [17], magic angle at 21.22 eV.

<sup>c</sup>Reference [17], magic angle at 40.81 eV.

<sup>d</sup>Reference [15],  $90^\circ$  angle at 40.81 eV.

<sup>e</sup>Reference [18], magic angle at 25 eV.

<sup>f</sup>Reference [16], magic angle at 21.22 eV.

all photon energies, then deviations from the geometric ratios are likely to be observed.

In conclusion, our study presents true branching ratios for the  $^3P_J$  fine-structure populations for both  $3p$  and  $3s$  photoionization of atomic chlorine. In contrast to previous measurements, which were subject to influences from nonisotropic angular distributions, these new data can be directly, and rigorously, compared with theoretical predictions. The  $3p$  ratios for Cl and the  $4p$  ratios for Br, which were measured very recently, agree well with the geometric ratios, which are based on Racah angular-momentum-coupling theory with the assumption of the single-particle approximation and the neglect of  $LS$  dependence in the dynamical matrix elements. The same geometric ratios are seen to be in accord with earlier measurements for the closed  $4d$  subshell in the open-shell atom Ag and for photodetachment data of  $O^-$  and  $S^-$ . By contrast, the  $3s$  ratios for Cl agree poorly with the geometric ratios. Although we expect less mixing of the  $3s$  states with  $nd$  states in the case of Cl than in Ar, where strong satellites arise as a consequence, there is

doubtless some mixing present. In fact, calculations in an eigenchannel  $R$ -matrix formulation give evidence for such interactions. However, even with the inclusion of these effects, as reported by Pan and Starace [5], the agreement between experiment and theory remains poor, suggesting the need for more extensive work both theoretically and experimentally.

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