A Critical Test of Many-Body Theory: The Photoionization Cross Section of Cl as an Example of an Open-Shell Atom

James A. R. Samson, Y. Shefer, and G. C. Angel
Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68588

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The present work reports the first absolute photoionization cross-section measurements for the open-shell atom chlorine. Measurements were made from the ^1S ionization threshold at 16.4 eV to 75 eV. Agreement with several calculations is good at the higher photon energies. We have observed a Cooper minimum at about 44 eV as predicted by theory. However, near threshold the various calculations differ considerably with each other and with the present results.

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Electron correlation in open-shell atoms is presently an important but difficult research field in theoretical atomic physics. The photoionization process is the more fundamental process to study electron correlations compared to any scattering process. In particular, the photoionization cross section of atomic chlorine has been chosen as a test case to develop the theory of atomic photoionization for open-shell atoms.[1-11] Therefore, the experimental investigation of the photoionization of an open-shell atom, such as Cl, has basic importance and will serve as a critical test for theoretical calculations. The only experimental cross-section measurement that has been made for Cl is the relative photoionization cross sections of Ruscic and Berkowitz in the autoionizing region from the ionization threshold at 956 to 755 Å ($^1S_0$ threshold).[12] In the present work we have measured the absolute cross sections of atomic chlorine from 158 to 767 Å by first measuring the relative values, which were then placed on an absolute basis by our normalizing the data to $\frac{1}{2}$ of the measured absolute molecular cross section,[13,14] then verifying that the results satisfied the oscillator sum rule for absorption.

The principle of our experimental technique is similar to that previously described for atomic oxygen.[15] Briefly, we studied Cl with a mass spectrometer and measured, in relative units, the number of Cl^+ ions produced per incident photon as a function of wavelength. At the low pressures used in the mass spectrometer this quantity is proportional to the photoionization cross section.

Atomic chlorine was produced in a microwave discharge by the dissociation of Cl_2. Approximately 20% molecular dissociation was produced when the Pyrex flow tube was coated with phosphorus pentoxide and subsequently exposed to the humidity in the laboratory. The Cl_2 pressure in the discharge tube was about 0.37 Torr. The discharged products were constrained to flow past a small orifice, 0.5 mm in diameter, leading to the ion chamber of the mass spectrometer.

A crucial part of the experiment was to keep the Cl number density constant. This was achieved by use of a reservoir of liquid Cl_2 which was maintained at 195 K by means of a trap with a dry ice and methanol mixture. The vapor pressure at this temperature was 127 Torr. The gas was allowed to flow into the discharge region through a glass capillary approximately 29 cm long and 1 mm in diameter. The pressure gradient thus set up a pressure of 0.37 Torr in the discharge tube.

Another crucial part of the experiment was to measure the intensity of the incident radiation. This was done by use of a calibrated photodiode, which was calibrated in absolute units by use of a double ion chamber[16] and in relative units by monitoring, simultaneously, the ion signal from a rare gas in the mass spectrometer and the response of the photodiode.[15]

Because a microwave discharge produces a mixture of Cl and Cl_2 we must take into account the presence of a false Cl^+ signal produced by dissociative photoionization of the molecule. We have shown previously for the case of atomic oxygen[15] that the relative photoionization cross section of an atom is given as

$$\sigma(\mathrm{Cl}) \propto (S_1' - \alpha S_1)(\eta/i), \qquad (1)$$

where i is the current from the photodiode that monitors the incident radiation, η is the photoelectric efficiency of the cathode, and S_1 and S_1' are the Cl^+ ion signals measured with the microwave power off and on, respectively. The parameter $\alpha = S_2'/S_2$, where S_2 and S_2' are the $Cl_2{}^+$ ion signals measured with the microwave power off and on, respectively. That is, α measures the degree of dissociation of Cl_2 produced by the microwave discharge. From the definition of the photoelectric efficiency, namely, the number of photoelectrons emitted from the photocathode per incident photon, it follows that the absolute intensity of the incident radiation I_0 is given by $I_0 = i/\eta e$, where e is the electronic charge. Thus, Eq. (1) simply expresses the fact that the cross section is proportional to the ratio of the number of Cl^+ ions produced per incident photon, corrected for any dissociative photoionization. Equation (1) is valid provided any recombination of atomic chlorine produces only Cl_2 and not another compound.[15] We scanned the mass spectrum of the discharged products but observed only Cl and Cl_2. The reported photoelectron spectrum[17,18] of Cl_2 at 584 Å shows no presence of excited-state Cl atoms. However, the authors do observe the presence of HCl.

Absolute photoionization cross sections of Cl_2 were measured from 158 to 800 Å with an accuracy of $\pm 3\%$. Details of these results are published separately.[14]

The photoionization cross sections of atomic chlorine are shown in Fig. 1. They were obtained by use of Eq. (1) and normalized to $\frac{1}{2}$ of the molecular cross sections in the spectral region between 300 and 450 Å. The molecular cross sections (divided by 2) are also shown in Fig. 1 and cover the range 158 to 500 Å. The deviation between the atomic and molecular curves starts at about 450 Å. The solid line represents the best fit to the data points and these values have been tabulated in Table I. The region below 350 Å is enlarged by a factor of 10 to show the presence of a Cooper minimum at 43.5 eV (285 Å).

The statistical errors were only about $\pm 5\%$, but the major scatter in the data points was caused primarily with variations in the value of α. As the phosphorus pentoxide coating aged, the amount of dissociation decreased, causing frequent renewals of the coating. The data represent the average of many runs with different coatings in which α ranged from 0.7 to 0.8. The scatter in the 600-Å region, of course, could be caused by autoionizing structure. These are expected in this general region for the excitation of a $3s$ electron, namely, the series, $3s^2 3p^5 \rightarrow 3s3p^5 np$. Brown, Carter, and Kelly[8] have calculated the energies of the first four members of the series. However, the positions, shown in Fig. 1 by the vertical dashed lines, do not cover the region of maximum scatter.

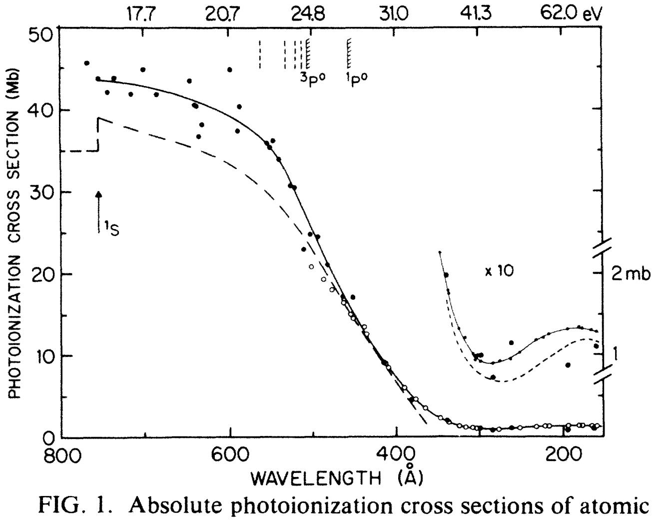

FIG. 1. Absolute photoionization cross sections of atomic chlorine as a function of wavelength. Experimental data: solid line and large solid circle, present data; open circle and small solid circle, present data for $\frac{1}{2}$ molecular cross section. Theoretical data: long dashes, Ref. 4; short dashes, Ref. 5. The vertical dashed lines represent a line series terminating at the $3P°$ state (Ref. 8).

The absolute accuracy of the averaged data is estimated to be about $\pm 8\%$. This includes an uncertainty of approximately $\pm 5\%$ in the normalizing process. At shorter wavelengths the cross sections (those based directly on $\frac{1}{2}$ the molecular cross section) have a precision of $\pm 3\%$.

A check on the absolute accuracy of the data was made by our determining the total oscillator strength for the absorption process. According to the Thomas-Reiche-Kuhn sum rule the total oscillator strength should equal the number of electrons in an atom. From the present data the oscillator strength between 158 and 755 Å is 4.44. From the results of Ruscic and Berkowitz[12] we estimate an oscillator strength of 1.11 from the ionization threshold to the ^1S level (755 Å). Between 0 and 158 Å the tabulated cross sections of Henke *et al.*[19] yield an oscillator strength of 10.94 giving a total continuum value of 16.49. There are few estimates of the discrete-line oscillator strengths leading up to the first ionization threshold. The critical compilation of discrete oscillator strengths by Wiese, Smith, and Glennon[20] lists seven transitions of the type $3p^5 \rightarrow 3p^4 4s$, which yield a total oscillator strength of 0.22. It is unlikely that the remaining discrete oscillator strengths will exceed about 0.5 on the basis of typical values for other atoms. Thus the total oscillator strength is within a few percent of the required value of 17. This confines our overall estimated error of $\pm 8\%$.

TABLE I. The photoionization cross section of atomic chlorine measured in megabarns (1 Mb $= 10^{-18}$ cm^2). The data were obtained from the smooth curve through the experimental points in Fig. 1.

Wavelength (Å)	Cross sections (Mb)	Wavelength (Å)	Cross sections (Mb)
158	1.29	475	20.2
175	1.32	500	25.8
200	1.30	525	32.2
225	1.19	550	35.7
250	1.02	575	38.0
275	0.90	600	39.4
300	0.94	625	40.6
325	1.40	650	41.6
350	2.50	675	42.4
375	4.60	700	43.0
400	7.50	725	43.4
425	11.0	755	43.6
450	15.3		

The photoionization cross sections for the $3p$ subshell have been calculated by Cherepkov and Chernysheva by use of the random-phase approximation with exchange.[3,4] Their results, using experimental values for the ionization thresholds, are shown in Fig. 1 by the dashed line (for wavelengths longer than 350 Å).[4] However, they have not included the coupling of the $3s$ to the $3p$ subshell. This omission causes the $3p$ cross section to decrease rapidly at shorter wavelengths. The inclusion of the coupling by Yarzhemsky *et al.*[5] produces a Cooper minimum and a subsequent maximum in the $3p$ cross section at shorter wavelengths. A similar curve is produced in the $3s$ cross sections but with slightly displaced minimum and maximum. The sum of their $3p$ and $3s$ calculations is shown by the dashed curve in the ×10 enlargment in Fig. 1. The experimental data (both small and large closed circles) are also shown in the enlargement and clearly exhibit a Cooper minimum at 43.5 eV (285 Å) in good agreement with theory. The detailed outline of this curve is made possible by the use of half of the measured molecular cross-section data (small solid-circle data points).

Figure 2 compares the theoretical geometric-mean total photoionization cross sections for the $3p$ subshell[6,8–10] (as presented in Ref. 10) with the present smoothed data. The calculated cross sections of Brown, Carter, and Kelly for the $3s$ subshell are also shown in the figure (enlarged by a factor of 2) to indicate, approximately, how much the calculated $3p$ cross sections should be increased for direct comparison with the experimental results below 500 Å. Because they used experimental ionization potentials for both their $3p$ and $3s$ calculations, their results were used in this wavelength region in preference to those of Yarzhemsky *et al.*[5] This particularly improves the $3s$ subshell results at threshold.[21] Although the addition of the $3s$ cross section further increases the magnitude of the theoretical curves above the experimental values at wavelengths shorter than 500 Å, there is still good overall agreement between theory and experiment. In fact, it brings the calculations of Cherepkov and Chernysheva (Fig. 1) into nearly perfect agreement with experiment between 400 and 500 Å.

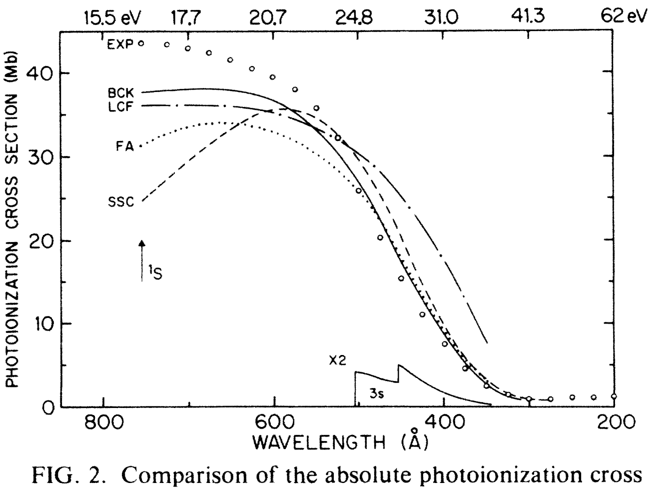

FIG. 2. Comparison of the absolute photoionization cross sections of atomic Cl with theoretical results. Experimental (EXP): open circle, present smoothed results from Table I. Theoretical: solid line, Ref. 8; dotted-dashed line, Ref. 6; dotted line, Ref. 9; dashed line, Ref. 10. The curve labeled ×2 represents the $3s$ subshell cross sections calculated by Brown, Carter, and Kelly (Ref. 8).

The early adaptation of the random-phase approximation with exchange calculations to Cl did not include interchannel coupling.[1] These calculations produced similar results to the Hartree-Fock calculations, which gave a very large cross section (~67 Mb) at the ^1S threshold. Subsequent calculations, including those shown in Figs. 1 and 2, have all used some type of interchannel coupling. The good agreement with experiment confirms the importance of the interchannel effects. However, there is still some disagreement between experiment and the various calculations at the ^1S threshold.

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