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Photoelectron angular distribution of $3s$ photoionization of atomic chlorine

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The photoelectron angular distribution asymmetry parameter β for $3s$ electrons of atomic chlorine has been calculated using the multiconfiguration Hartree-Fock method for both bound and continuum wave functions. It is determined in the electric dipole approximation within the framework of the angular-momentum-transfer formulation. The effects of electron correlation are investigated, and it is shown that electron correlations are very important for β values corresponding to both ^3P and ^1P ionic states. Our results confirm the recent experimental prediction that β for s subshell photoionization in open-shell atoms, is, in general, term and photon energy dependent and, in addition, in the case of chlorine $3s$ photoionization, β has minima for both terms of Cl^+ $3s(^3P,\,^1P)$, in qualitative agreement with experiment. However, our calculation of β for Cl^+ $3s(^3P,\,^1P)$ channels demonstrates that interchannel coupling should be included in order to achieve quantitative agreement with experiment.

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Experiments on measurements of angular distributions of photoelectrons, or the photoelectron asymmetry parameter β provide data not only on the relevant transition amplitudes but also on their relative phases. These data also supply information on the initial and final states of the target as well as dynamic information on the interaction of the photoelectrons with the resulting ion. The extraction of information by a theoretical calculation is a good test of any theory.

The well-known expression for angular distribution of photoelectrons is given by

$$\frac{d\sigma}{d\omega}=\left(\frac{\sigma}{4\pi}\right)[1+\beta P_2\cos(\theta)].$$

In general, the angular distribution of photoelectrons varies as a function of photon energy due to interference of two possible partial waves. But there are exceptions. In the case of the photoionization of s-subshell electrons in closed-shell atoms, nonrelativistically, the angular distribution parameter β becomes equal to two, independent of the photon energy [1]. This is because in this case only one partial wave is allowed in the dipole approximation. But in the case of most open-shell atoms, this result is no longer true although there is only one partial wave. Generally, in open-shell atoms there is more than one final-state channel due to the nonrelativistic electron-ion interactions. Interference between these final-state channels leads to a β dependence on photon energy as well as on term values.

Recently there has been a growing interest in the photoionization of open-shell atoms both experimentally and theoretically. However, the photoionization from the $3s$ subshell of open-shell atomic chlorine has received relatively little theoretical attention due to the target and the remaining core being open shell. Many years ago, Starace, Rast, and Manson [2] calculated the angular distribution parameter β for $3s$-subshell photoionization of atomic chlorine using single configuration restricted Hartree-Fock (HF) continuum orbitals, where electron correlation is completely neglected. They predicted a term and photon energy dependence of β. These predictions had gone unverified for more than 20 years. This was partly due to the difficulty of producing a good atomic beam of an open-shell atom such as chlorine, and in part to the relatively small photoionization cross sections of s-subshell electrons. Very recently, Whitfield *et al.* [3] reported measurements on the photoelectron angular distribution parameter β of the $3s$-subshell photoionization of atomic chlorine over the photon energy range 29–70 eV using electron spectrometry in conjunction with synchrotron radiation. Their results confirm the basic theoretical predictions of Starace, Rast, and Manson [2] that β for s-subshell photoionization in open-shell atoms, is, in general, term and photon energy dependent. However, their measurements for the Cl^+ $3s(^3P,\,^1P)$ ionic channels demonstrate that there are significant qualitative and quantitative discrepancies between the existing theory and their experiment. Experimentally, minima are found in β for the both Cl^+ $3s(^3P)$ and Cl^+ $3s(^1P)$ cases, but theory [2] finds minima only in the Cl^+ $3s(^3P)$ case, not in the Cl^+ $3s(^1P)$ case. In addition, the magnitude and location of the minimum in the (^3P) case observed by experiment [3] do not agree with the existing theory [2].

As the angular distribution parameter β depends on the dipole matrix elements between the initial and final states as well as on their relative phases, these quantities must be calculated very accurately in order to test the discrepancies between theory and experiment. In this paper we present a theoretical investigation of the $3s$ photoionization of the open-shell atomic chlorine atom to understand, and potentially remove, the discrepancy between the existing theory and the experiment. The calculation is carried out using the multiconfiguration Hartree-Fock method for both bound [4] and continuum wave functions [5], which has proved to be very efficient for including the electron correlation effects into the wave function. We consider both electron correlation and polarization effects in the initial state, the final ionic states, and the final continuum states through the configuration interaction procedure. We report here on the calculation of the asymmetry parameters $\beta(^3P)$ and $\beta(^1P)$ corresponding to two ionic term thresholds. The results are obtained in *LS* coupling, spin orbit and other relativistic effects are not

TABLE I. Comparison of energy levels (ionization thresholds) of Cl$^+$ $3s3p^5$ in eV relative to Cl $3s^23p^5(^2P)$, with experiment [3].

State	Calculated (eV)	Experiment (eV)
^3P	24.52	24.54
^1P	28.89	27.30

considered. To calculate the β parameter we use the angular-momentum formulation of Dill and Fano [6] and the *LS* coupling form of Dill, Manson, and Starace [7].

In this investigation we consider the $3s$-electron photoionization from the ground state Cl $3s^23p^5(^2P)$ of the chlorine atom. The photoionization processes are described by

$$\hbar\omega + \text{Cl}\ \ 3s^23p^5(^2P)$$
$$\rightarrow \text{Cl}^+3s3p^5(^3P)+e^-(kp)(^2D,\ ^2P,\ ^2S)$$
$$\rightarrow \text{Cl}^+3s3p^5(^1P)+e^-(kp)(^2D,\ ^2P,\ ^2S).$$

Initially we performed a HF calculation with the core orbitals prepared from the Cl$^+$ $3s3p^5(^3P)$ core. With these core orbitals we calculated the initial, final ionic states, and the final *LS* photoionized states and obtained β using the angular-momentum-transfer formulation stated above. Since, in the photoionization of open-shell atom electron correlation and polarization effects are extremely important, a variational calculation is performed using the multiconfiguration Hartree-Fock (MCHF) method that has the potential of taking into account very accurately the electron correlation and polarization effects completely *ab initio* through the configuration-interaction procedure. We first calculated the $1s$, $2s$, $2p$, $3s$, and $3p$ wave functions of the Cl$^+$ $3s(^3P)$ core in the HF approximation. Then we prepared a configuration set for the initial Cl (^2P) state by including all the configurations obtained by single and double replacement of the two outermost orbitals of the initial-state configuration with the excited orbitals $3d$, $4s$, and $4p$. We computed all the excited $3d$, $4s$, and $4p$ orbitals variationally in the MCHF approximation with the core orbitals obtained from the relaxed Cl$^+$ $3s(^3P)$ ion core. The final core ionic state $3s3p^5(^3P,\ ^1P)$ wave functions are calculated similarly in the MCHF approximation using a large set of configurations. The final continuum state wave functions for different final *LS* states corresponding to each ionic state are calculated using the MCHF method for the continuum wave function [5]. Each of the final *LS* state wave functions is calculated separately corresponding to each ionic core state. For each of these different final *LS* states separate configuration sets are generated again by single and double replacements of $3s$ and $3p$ outermost orbitals with $3d$, $4s$, and $4p$ excited orbitals. Some of the excited bound orbitals are optimized along with the continuum orbital simultaneously for each kinetic energy of the photoelectron. This takes into account polarization effects of the core due to the continuum electron. In all cases, the core orbitals were kept fixed at the HF Cl$^+$ (^3P) value. It should be pointed out that because chlorine is an open-shell atom, a large number of configurations contributed to the initial as well as to each of the final *LS* states. Special effort was made to make the wave functions accurate and *ab initio* in each of these cases. These wave functions are used to

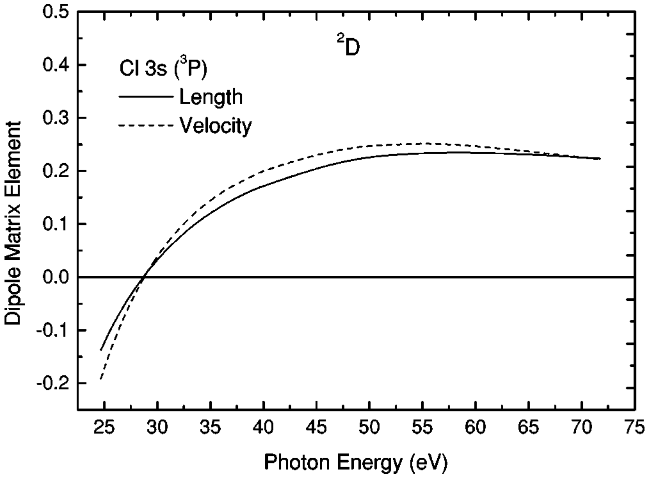

FIG. 1. Dipole matrix elements in both length and velocity forms as a function of photon energy for the ^2D final state corresponding to the Cl$^+$ $3s(^3P)$ ionic state.

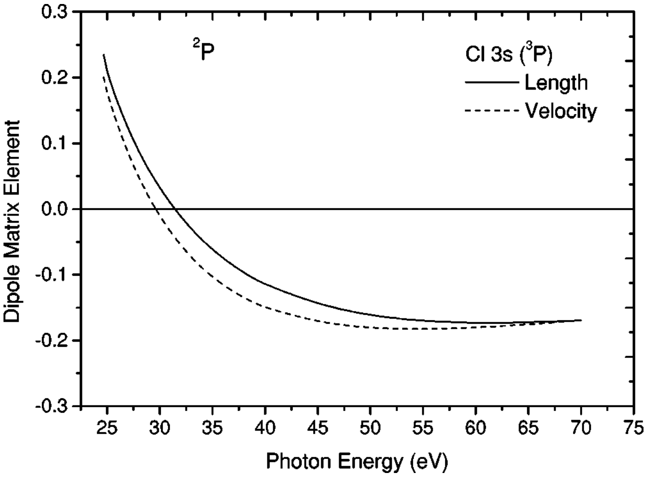

FIG. 2. Same as Fig. 1 but corresponding to the ^2P final state.

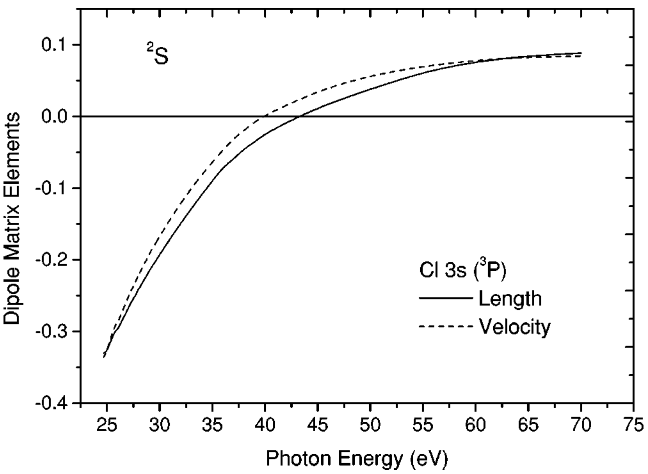

FIG. 3. Same as Fig. 1 but corresponding to the ^2S final state.

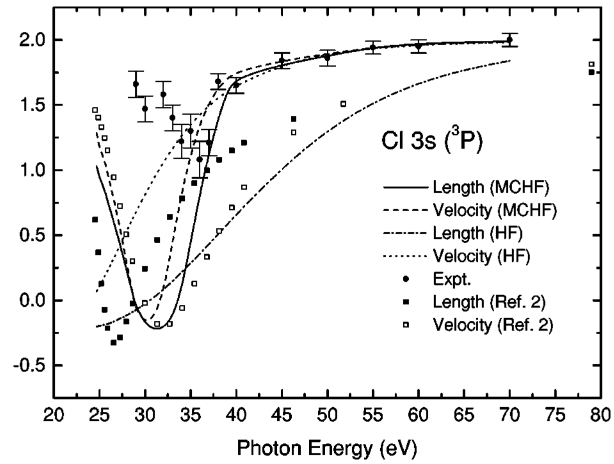

FIG. 4. Theoretical and experimental β values corresponding to the Cl^+ $3s(^3P)$ ionic state as a function of photon energy.

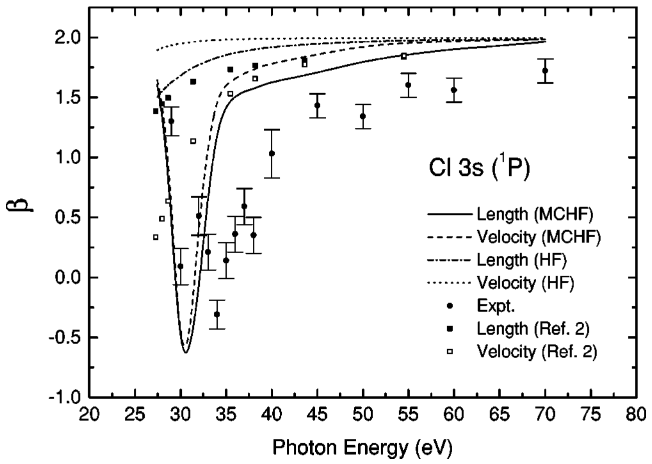

FIG. 5. Theoretical and experimental β values corresponding to the Cl^+ $3s(^1P)$ ionic state as a function of photon energy.

calculate the dipole transition matrix elements between the initial and the final states. Finally, the asymmetry parameter $\beta(^3P)$ and $\beta(^1P)$ corresponding to two ionic term levels Cl^+ $3s3p^5(^3P,\ ^1P)$ are calculated using the dipole matrix elements and the relative phases.

The determination of the asymmetry parameter corresponding to each of the ionic states requires correct evaluation of the scattering amplitudes that involve dipole matrix elements. The dipole matrix elements are determined by the initial- and the final-state wave functions. One way to ensure the quality of the wave functions required for dipole matrix elements is to check the threshold energies. In Table I we present threshold energies for the two ionic states along with the experimental data for comparison. The agreement is excellent.

The next step is to examine the behavior of the dipole matrix elements as a function of the photon energy. In Figs. 1, 2, and 3 we plot the dipole matrix elements in both length and velocity forms as a function of photon energy for the three final ^2D, ^2P, and ^2S states corresponding to the ^3P ionic state. It is found that matrix elements in each of these cases pass through zero as a function of photon energy. This indicates that there should be a Cooper minimum [8] in the asymmetry parameter at an energy depending on the relative position of the zeros in the dipole matrix elements.

Our calculated MCHF β values in both length and velocity forms corresponding to Cl^+ $3s(^3P)$ and Cl^+ $3s(^1P)$ ionic states as a function of photon energy are presented in Figs. 4 and 5. Also shown in the figures are the recent experimental data reported by Whitfield *et al.* [3]. Both β values clearly show a dependence of β on the terms of Cl^+ $3s$ as well as on the photon energy, in qualitative agreement with experiment. It can be noticed from Figs. 4 and 5 that, corresponding to each of the ionic states, the β parameter shows a minimum as a function of photon energy, also in agreement with experiment [3]. In the ^3P ionic case, the magnitude of the dip of the minimum as well as the location of the minimum are much lower than those obtained by experiment. In the case of the ^1P ionic state there is better agreement with experiment, but the dip of the minimum and its position are shifted towards the threshold compared to experiment. As seen from the figures, the discrepancies between the present theory and the experiment are in the magnitude of the dip in the minima and their position. In the case of ^3P, the experiment found the magnitude of the minimum to be 1.08 and its location at a photon energy 36 eV, while the current theory shows a minimum at 31 eV and its magnitude to be -0.22 in the length form. On the other hand, in the case of the ^1P case, calculated length values of the magnitude and location are, respectively, -0.08 and 31 eV whereas corresponding experimental values are -0.31 and 34 eV. One of the reasons for the differences in the depths of the minima may be due the effect of instrumental resolution (30 meV) on the experimental data. It can often happen that features in the theoretical calculation are more narrow than features in the experiment because the latter are smoothed by the instrumental resolution.

In order to determine the effect of electron correlation on the β values we also included in Figs. 4 and 5 our calculated HF results for the β parameter corresponding to both ^3P and ^1P ionic states. They did not show any Cooper minima in the β parameter. For comparison we also presented existing simple HF results [2] in Figs. 4 and 5. The reason that these HF results [2] show minima in the ^3P case may be due to the use of the continuum orbitals calculated in the restricted HF approximation. The presence of the Cooper minima can also be identified simply by looking into the dipole matrix elements as a function of photon energy. To have a minimum in the β parameter, the matrix elements have to pass through zero. It should be mentioned that in this particular study we found that the electron correlations are very strong in both the initial and the final states, and without these the minima in the β values could not be obtained.

Although we have taken into account electron correlation effects very efficiently in both the initial and the final states through the configuration-interaction procedure, there is still quantitative disagreement between the present theory and the recent experiment. The possible reason for this discrepancy may be accounted for due to the strong interchannel coupling between the continuum channels, including ionization with excitation. In the present calculation, the effect of interchannel coupling has not been taken into account through the MCHF approximation. Recently, the MCHF method for the continuum wave function has been extended to include interchannel coupling between the open channels, and refined calculations that include interchannel coupling are underway.

We have presented a theoretical confirmation of the term and photon energy dependence of the photoelectron asymmetry parameter β of the $3s$-subshell electrons in the open-shell chlorine atom arising solely from the interference of the final-state channels. One of the most important motivations of the present calculation was to examine the presence of the minima in the β values corresponding to ^3P and ^1P ionic terms in order to confirm the experimental observations [3]. While the earlier theoretical investigations [2] using the single configuration restricted HF approximation obtains a minimum only in the ^3P case, and no minimum in the ^1P case, the present calculation verifies the presence of the minima in both the ^3P and ^1P cases. We included a large number of configurations in both the initial and each of the final LS states to obtain convergence in the β values. This study clearly demonstrates the importance of electron correlation in the β values in the present calculation. The discrepancies that still exist are the magnitude and location of the minimum in the β values. This may be attributed to the presence of interchannel interaction, which could not be taken into account in the present study. Future calculation with inclusion of interchannel coupling may bring theory and experiment close together and thus help to gain a clear understanding of the dynamical processes involved in electron dynamics in the photoionization of open-shell atoms.

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