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Photoionization cross section with excitation of neutral argon

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Many-body perturbation theory has been used to calculate photoionization cross sections with excitation of neutral argon leaving the ion in $3s^23p^4(^1D)md(^2S)$ levels. Correlations both in the final state and ground state are included. Calculated cross sections for $3s^23p^6 \rightarrow 3s3p^6\epsilon p$ and $3s^33p^6 \rightarrow 3s^23p^4(^1D)md(^2S)\epsilon p$ excitations were used to determine the satellite intensities, which are compared with photoelectron measurements and other calculations.

There has been considerable interest among both theorists and experimentalists in studying the satellite of argon following ionization in the $3s$ shell. It is now many years since Minnhagen[1] explained $md(^2S)$ satellites due to the strong interaction in the final ionic states between the $3s3p^6$ and $3s^23p^4md$ series.

This satellite spectrum has been observed by photoelectron[2-7] (γ,e) and electron-momentum[8-11] $(e,2e)$ spectroscopic methods, and currently disagreement exists between them as to the relative intensities of satellite lines. Attempts were made by both theorists[12] and experimentalists[13] to resolve the disagreement.

Inconsistencies also exist between different theoretical calculations. The predicted relative intensities of the $3d(^2S)$ line by Martin, Kowalczyk, and Shirley,[14] McCarthy, Uylings, and Poppe,[15] Williams,[16] Dyall and Larkins,[17] and Smid and Hansen[18-22] agree approximately with photoelectron experimental results, but there are variations among different calculations. These studies are basically configuration interaction calculations. In one of the papers of Smid and Hansen[20] the energy dependence of relative intensities of satellites is included by calculating the $3s$ dipole matrix elements, and results are in good agreement with photoelectron experiments. In a configuration-interaction calculation performed by Mitroy, Amos, and Morrison[23] the basis set consists of $3d$ and $4d$ orbitals and an additional $\bar{d}$ orbital taken to approximate the high-d orbitals including continuum. Their calculations agree with $(e,2e)$ measurements but not with the photoelectron experiments.

Amusia and Kheifets[12] argued that influence of ground-state correlations on photoionization is more important than on the $(e,2e)$ reaction, and they define a new spectroscopic factor for photoionization which includes some effects of ground-state correlations. The calculated relative intensities agree fairly well with experimental[2-7] results in the high-energy limit. Recent calculations by Hibbert and Hansen[22] include extensive configuration interaction effects, and are in very good agreement with recent experiments by Svensson, Helenelund, and Gelius[7] at 1487 eV, but somewhat differ from earlier calculations.[14-22]

In this work we calculate absolute cross sections for photoionization with excitation, leaving the ion in the $3s^23p^4md(^2S)$ level. These calculations, carried out with many-body perturbation theory (MBPT),[24-26] include both ground- and final-state correlations. The relative intensities of satellites are obtained from ratios of the absolute cross sections. The channels included are given in Table I, along with photoionization threshold energies taken from experiment.[7,27] In Table I for comparison we also give our calculated threshold energies obtained by differences between Hartree-Fock calculations for the ground state and the ionic levels (ΔSCF). Using experimental energies corresponds to a summation of higher-order terms in the perturbation expansion.[28] The $3s3p^6$ orbitals were obtained from a Hartree-Fock[29] (HF) calculation, and md orbitals of $3s^23p^4(^1D)md$ were calculated from frozen-core HF calculations with the core taken from a HF calculation for $3s^23p^4(^1D)$.[18] All md orbitals are mutually orthogonal since they are calculated in the same potential. The configuration interaction calculation for $3s3p^6$ and $3s^23p^4(^1D)md$ was performed by using ten d orbitals ($m=3$ to 12). Overlap integrals were included in calculating interaction between $3s3p^6$ and $3s^23p^4(^1D)md$. The influence of the ϵd continuum was not explicitly included but is roughly represented in the highest-d orbital. The mixing coefficients were used to calculate appropriate potentials for bound and continuum states of $3s3p^6(^2S)\epsilon p$ and $3s^23p^4(^1D)md(^2S)\epsilon p$. The symbol ϵ represents both bound and continuum states. The excited ϵd and ϵs states of $3s^23p^5(^2P)\epsilon d$ and

TABLE I. Threshold energies for the excitations considered. The photoionization threshold energies were taken from experiment.

Channel	Threshold (eV)	ΔSCF (eV)[a]
$3s^23p^5(^2P)\epsilon d/\epsilon s$	15.76[b]	14.80
$3s3p^6(^2S)\epsilon p$	29.24[b]	33.20
$3s^23p^4(^1D)3d(^2S)\epsilon p$	38.60[c]	38.96
$3s^23p^4(^1D)4d(^2S)\epsilon p$	41.21[c]	40.59
$3s^23p^4(^1D)5d(^2S)\epsilon p$	42.67[c]	41.45
$3s^23p^4(^3P)4p(^2P)\epsilon d/\epsilon s$	35.64[c]	38.31
$3s^23p^4(^1D)4p(^2P)\epsilon d/\epsilon s$	37.15[c]	39.14
$3s^23p^4(^1S)4p(^2P)\epsilon d/\epsilon s$	39.57[c]	41.54

[a]Difference between Hartree-Fock calculations of ionic core level and ground state $3s^23p^6(^1S)$.
[b]Moore *et al.* (Ref. 26).
[c]Svensson *et al.* (Ref. 7).

$3s^2 3p^5(^2P)\epsilon s$ were calculated in the respective HF potentials. The same ϵd and ϵs states are used for the states of $3s^2 3p^4(^3P, ^1D, ^1S)4p(^2P)\epsilon d$ and $3s^2 3p^4(^3P, ^1D, ^1S)4p(^2P)\epsilon s$.

Our coupled equations method[30] was used to couple the interactions between single and double excitation channels (given in Table I). The $2p^5 3s^2 3p^6 \epsilon d/\epsilon s$ channels are not included since preliminary calculations showed that interactions between them and other channels considered are small. We corrected the ϵd (ϵs) wave functions used for $3s^2 3p^4(^3P, ^1D, ^1S)4p(^2P)\epsilon d$ (ϵs) by including the difference between the potentials appropriate for $3s^2 3p^4(^3P, ^1D, ^1S)4p(^2P)\epsilon d$ (ϵs) and $3s^2 3p^5 \epsilon d$ (ϵs) in the coupled equations.

We present our results along with experimental values for the $3s^2 3p^4(^1D)md(^2S)\epsilon p$ ($m=3,4,5$) cross sections in Fig. 1. Experimental values were determined from our calculated $3s$ cross section, which agrees with the experimental results,[4] and the experimental relative intensities.[6] For the $3s^2 3p^4(^1D)3d(^2S)\epsilon p$ channel length and velocity cross sections are in close agreement. The resonances in the range 35.0 to 40.6 eV are the higher members of the Rydberg series of $3s^2 3p^4(^1D)4d(^2S)np$ and $3s^2 3p^4(^1D)5d(^2S)np$. The cross section, which has a minimum at 45.0 eV, gradually increases and then begins to decrease in agreement with experimental observations by Adam, Morrin, and Wendin.[4] Since length and velocity results are very close for the $3s^2 3p^4(^1D)4d(^2S)\epsilon p$ and the $3s^2 3p^4(^1D)5d(^2S)\epsilon p$ cross sections, only length forms are shown. In the $4d$ case, preliminary experimental results by Samson, Chung, and Lee[31] are in closer agreement with the calculations than previous experimental results.[6] Our calculated cross sections do not include effects of relaxation and polarization, and are probably less accurate within 5.0 eV of threshold than at higher energies.

The shape of the $3d(^2S)$ cross section is very similar to that of the $3s3p^6(^2S)$ cross section,[4] and we interpret this as due to the fact that the coupling with the $3s3p^6\epsilon p$ channel is driving the $3d(^2S)\epsilon p$ channel. It is also interesting to note the strong effects on the $3s3p^6\epsilon p$ channel due to coupling with the $3p^5\epsilon d/\epsilon s$ channels.[32] We believe that the $4d(^2S)$ and $5d(^2S)$ cross sections would also show the characteristic shape of the $3s3p^6(^2S)$ cross section if the oscillator strengths were plotted into the region of bound Rydberg states. Very close to threshold in the $4d(^2S)$ cross section there are $3s^2 3p^4(^1D)5d(^2S)np(^1P)$ resonances due to high-lying np Rydberg states but these are not shown. There should also be resonance structure in the $5d(^2S)$ cross section but we did not obtain this structure because we did not include the $6d(^2S)$ channel.

An approximation to the relative intensity for a given satellite is the ratio of the squared coefficient of $3s3p^6$ in the wave function of the configuration-mixed $3s^2 3p^4(^1D)md$ state to that for the configuration-mixed wave function of $3s3p^6$.[18] This result depends only on configuration mixing in the ion and is independent of photon energy. Our values calculated this way for the satellites $3d(^2S)$, $4d(^2S)$, and $5d(^2S)$ are 14.7, 7.7, and 4.4, respectively. The calculated relative intensities, including the effects of ground-state correlations and final-state correlations, are given in Table II at photon energies for which measured values exist. Since length and velocity results are very close, only the length results are shown. Our relative intensity for a given satellite is the ratio of the cross section of the satellite to the cross section of the $3s$ main line in percent. Experimental values are taken from Refs. 2–7. The calculated values of Smid and Han-

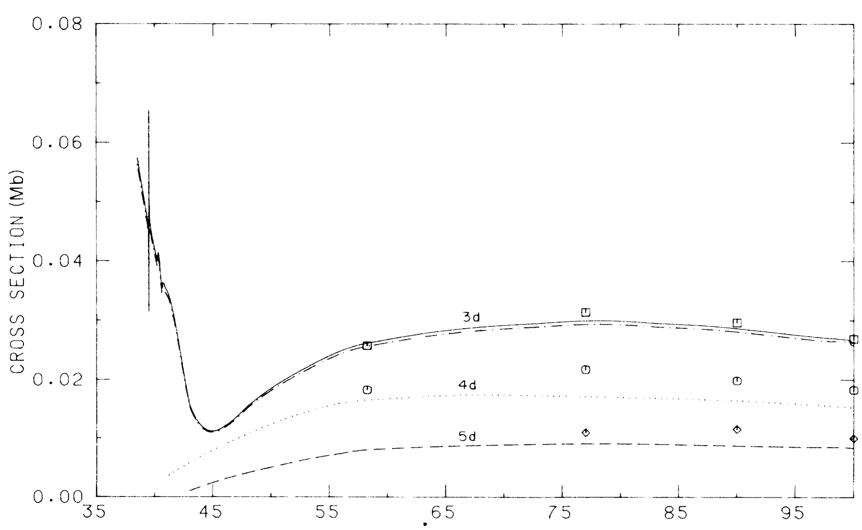

FIG. 1. Photoionization cross sections of $3s^2 3p^4(^1D)md(^2S)$ satellites. Solid line (dashed-dotted line) is the cross section of $3d(^2S)$ satellite in length (velocity) formalism. The dotted line and the dashed line are the cross sections of $4d(^2S)$ and $5d(^2S)$ in length formalism. ◻, ○, ◇ give the "experimental" cross sections of $3d(^2S)$, $4d(^2S)$, and $5d(^2S)$ satellites. The "experimental" values were determined using the experimental relative intensities of Ref. 6 and our calculated $3s$ cross section.

TABLE II. Satellite intensities relative to the 3s main line in percent. Footnotes a, e, f, and j refer to experimental work; b, c, d, g, h, and i refer to theoretical work. Error bars on the last significant number of each value are given in parentheses.

	$3p^4(^1D)3d(^2S)$		$3p^4(^1D)4d(^2S)$		$3p^4(^1D)5d(^2S)$	
Energy (eV)	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
58.3	17(1)[a]	17.1[b]	10(2)[a]	10.2[b]	4(2)[a]	5.3[b]
		17.6[c]		9.7[c]		5.5[c]
		15.7[d]		8.3[d]		4.6[d]
77.0	19.0[a]	16.7[b]	8(2)[a]	9.4[b]	6.0(6)[e]	5.1[b]
	17.2[e]	17.3[c]	11.9(6)[e]	9.5[c]		5.4[c]
		16.1[d]		8.7[d]		4.9[d]
90.0	17.0(8)[e]	16.1[b]	11.4(8)[e]	9.4[b]	6.6(8)[e]	5.1[b]
		16.8[c]		9.2[c]		5.2[c]
100.0	16.6(8)[e]	16.0[b]	11.3(8)[e]	9.4[b]	5.8(8)[e]	5.2[b]
		16.6[c]		9.0[c]		5.1[c]
110.0	16.1(8)[e]	15.6[b]	11.7(8)[e]	9.3[b]	6.4(8)[e]	5.0[b]
		16.5[c]		9.0[c]		5.1[c]
120.0	15.4(6)[e]	14.9[b]	11.2(6)[e]	9.2[b]	5.4(6)[e]	4.9[b]
		16.4[c]		9.0[c]		5.1[c]
151.0	15(2)[f]	14.6[b]	8(3)[f]	9.0[b]		4.7[b]
		15.9[c]		8.5[c]		4.8[c]
		15.0[d]		8.0[d]		4.5[d]
1254.0	15(2)[f]	13.9[b]	7(3)[f]	7.6[b]		4.4[b]
		13.5[g]		6.9[g]		3.8[g]
		18.9[h]		8.9[h]		2.5[h]
		18.1[i]		9.2[i]		3.4[i]
1487.0	19(2)[f]	14.1[b]	6(3)[f]	7.7[b]	4.1(3)[f]	4.5[b]
	18.6(5)[j]	13.5[g]	9.4(4)[j]	6.9[g]		3.8[g]
		18.9[h]		8.9[h]		2.5[h]
		18.1[i]		9.2[i]		3.4[i]

[a]Adam *et al.* (Refs. 3 and 4).
[b]This work (since length and velocity results are very close, only the length results are given).
[c]Smid and Hansen (length results) (Ref. 20).
[d]Smid and Hansen (velocity results) (Ref. 20).
[e]Kossmann *et al.* (Ref. 6).
[f]Spears *et al.* (Ref. 2).
[g]Smid and Hansen (Ref. 19).
[h]Amusia and Kheifets (Ref. 12).
[i]Hibbert and Hansen (Ref. 22).
[j]Svensson *et al.* (Ref. 7).

sen[19,20] are given in both length and velocity forms. We have also included a comparison with very recent calculations by Hibbert and Hansen[22] and by Amusia and Kheifets.[12] These results are expected to be accurate at high energies, and we have listed them in Table II at the two highest energies.

Our results show a slight decrease of relative intensities with increasing photon energy except at 1487 eV. Such a decrease was observed by Adam *et al.*[4] and Kossmann, Krassig, Schmidt, and Hansen.[6]

When we calculate relative intensities of satellites by only including final-state correlations, our results agree with those of Smid and Hansen[20] within a few percent but not as well with the more extensive recent configuration-interaction calculations of Hibbert and Hansen.[22] Inclusion of ground-state correlations reduced our discrepancy between length and velocity results by moving the velocity results closer to the length results. We notice that our final results (given in Table II) calculated by including the ground-state correlations and the final-state correlations for both the 3s main line and the satellite lines, do not differ considerably from those calculated, which only include final-state correlations.

In conclusion, we have calculated absolute photoionization with excitation cross sections for neutral argon, leaving the ion in $3s^2 3p^4(^1D)md(^2S)$ levels. The calculations include effects of both ground-state and final-state correlations. The cross sections were used to determine relative intensities of the $md(^2S)$ satellites relative to the $3s3p^6(^2S)$ main line. We found only a slight influence of ground-state correlations on the relative intensities, but a significant effect on the absolute cross sections.

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