Calculations of photoionization with excitation for Ca using the R-matrix approach

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Calculations of photoionization accompanied by excitation are reported for Ca using the R-matrix approach. Cross sections for leaving the Ca^+ ion in the states $3p^6 4s$, $3p^6 3d$, and $3p^6 4p$ are presented from the $4p$ threshold to a photon energy of 26 eV. Extensive configuration-interaction wave functions are used to describe both the initial and final states, and coupling between continua based on different thresholds is also included. The results differ considerably from previous calculations where coupling between the continua has been neglected. We show that in particular the $4s^2 \rightarrow 4s\epsilon p$ cross section is very sensitive to a number of factors. It is predicted that the $3d$ photoelectron satellite will be stronger than the main line ($4s$) from below the $4p$ threshold up to approximately 12 eV. No experimental measurements exist at the moment below 21.22 eV. At this energy there is reasonable agreement between the different calculations and with experiment.

I. INTRODUCTION

A number of calculations of the photoabsorption cross section of the neutral Ca atom have been published during the last few years. Altun, Carter, and Kelly[1,2] and Scott, Kingston, and Hibbert[3] have published calculations for the resonance region below the second, $3p^6 3d$, and third, $3p^6 4p$, thresholds with emphasis on the resonance structure in this region. This subject has been discussed in a number of earlier papers which are referenced in Refs. 1–3.

More recently, Cowan, Hansen, and Smid[4] and Altun and Kelly[5] have considered the region from the $3p^6 4p$ threshold (at 9.25 eV), to 28, and 50 eV, respectively, a region which has not been explored in any detail before. The emphasis in these papers is on the cross sections for photoionization with accompanying excitation to the $3d$ or $4p$ states of the ion compared to the cross section for leaving the ion in the $3p^6 4s$ ground state.

Altun and Kelly[5] considered also the region around 31.4 eV where the $3p \rightarrow 3d$ resonance occurs.[6] The photoelectron spectrum has recently been measured over selected resonances in this region by Bizau *et al.*[7] and found to be very complex.

However, interesting effects are also expected below the $3p \rightarrow 3d$ resonance region. In both Refs. 4 and 5, it was found that in the energy region close to the $4p$ threshold the so-called satellites in the photoelectron spectrum associated with the ionic $3d$ and $4p$ states were stronger than the main line associated with the ionic $4s$ ground state. There was reasonably good agreement between the two calculations with regard to the cross section for leaving the ion in the $3d$ state while the cross sections for leaving the ion in the $4s$ and $4p$ states differed appreciably, particularly in the energy region below 20 eV. The methods used in the two calculations were quite different. Cowan *et al.*[4] employed the configuration interaction (CI) techniques developed by Cowan[8] which are based on discretizing the continuum while Altun and Kelly[5] used the many-body perturbation theory (MBPT). Due to the complexity of the physical problem neither of the calculations were claimed to be of high accuracy.

Only one experimental measurement[9] exists in the energy region of interest here, namely one using the He I 21.22 eV resonance radiation, and at this energy the two calculations were in quite good agreement with each other although not with the experiment. However, the electrons were detected at 90° relative to the incoming photon and a measurement at the magic angle or a calculation of the angular asymmetry factors therefore was necessary in order to decide whether the disagreement is real.

There is thus a need for an improved calculation in order to decide which of the two previous calculations (if either) is correct close to the $4p$ threshold and a calculation of the angular asymmetry factors at 21.2 eV in order to allow an unambiguous comparison with experiment.

In this paper we report a calculation of the photoionization cross sections leaving the ion in the $4s$, $3d$, or $4p$ states for photon energies between 9.25 and 26 eV using the R-matrix approach.[10] This method allows the inclusion of coupling between the continuum channels based on different thresholds, which was neglected in the previous calculations, and we show that this coupling is very important near threshold. The coupling between the $4s\epsilon p$ and $4p\epsilon l$ channels is particularly important and it leads to results which, below 20 eV, are quite different from those obtained in both of the previous calculations. On the other hand, there is reasonable agreement between the three calculations for the $3d\epsilon l$ cross section. Angular asymmetry factors and a comparison with experiment are also reported.

II. CALCULATIONS

The calculations reported here form an extension of the work by Scott *et al.*[3] for the energy region below the $4p$ threshold. We have used the same description of the three Ca^+ states $3p^64s$, $3d$, and $4p$ as used in that work where details can be found. The cross sections were calculated using the R-matrix package[11] adapted to the CRAY-1 computer at the University of London Computing Center, and to the CYBER 205 installed at the Computer Center SARA in Amsterdam. The calculations, which are carried out in LS coupling and neglecting spin-orbit interaction, include the five continuum channels $4s\epsilon p$, $3d\epsilon p$, $3d\epsilon f$, $4p\epsilon s$, and $4p\epsilon d$ and the coupling between them. Also, a considerable amount of correlation in the initial and final state is included as described by Scott *et al.*[3]

In order to understand the differences between the previous calculations a number of auxiliary calculations have been made. The main improvement in the present calculations is the inclusion of the coupling between the continua based on different thresholds. Cowan *et al.*[4] found that the effects of this coupling is small if it is the only correlation effect present in the final state but they noted that this result might change when additional correlation effects are included. However, the methods used by these authors in conjunction with the limitations of the smaller computer available at the time did not allow *both* correlation in the final state and coupling between the continua to be included. Coupling between the continua was not included in the MBPT calculation either.[12].

Four different sets of calculations have been carried out. In the first calculation, designated I, we used a single-configuration Hartree-Fock (HF) description of the ionic states $3p^64s$, $3d$, and $4p$ and , using the same orbitals, we constructed a Ca I ground state of the form $\alpha_1 | 3p^64s^2\rangle + \alpha_2 | 3p^63d^2\rangle + \alpha_3 | 3p^64p^2\rangle$ without taking core polarization into account. In the final state we included terms of the form $3p^5nln'l'n''l''$. This is essentially the approach adopted by Cowan *et al.*[4] and reasonable agreement is obtained with their results. The only channel coupling included is that between the two $3d\epsilon l$ channels and that between the two $4p\epsilon' l$ channels.

In the second set of calculations, designated II, we retained the same initial and final states but coupling between the five channels $4s\epsilon_1 p$, $3d\epsilon_2 p$, $3d\epsilon_2 f$, $4p\epsilon_3 s$, and $4p\epsilon_3 d$ was included.

The third set of calculations, III, used the initial and final state wave functions constructed by Scott *et al.*[3] These wave functions allow for correlation including core polarization effects in both states. As in I, the only channel coupling included was that between the two $3d\epsilon l$ channels and that between the two $4p\epsilon' l$ channels.

In the fourth set of calculations, IV, we again used the wave functions of Scott *et al.*[3] but in this case the coupling between all five continuum channels was included.

It should be kept in mind that the most important correlation effect, the admixture of $4p^2$ and $3d^2$ into the $4s^2$ ground state, is included even in the simplest calculation (I). Use of the correlated ionic basis states instead of the HF basis states and including core polarization in otherwise equivalent calculations introduces an additional correlation effect which for the purposes of the following discussion we will call "full correlation."

III. IMPORTANCE OF DIFFERENT APPROXIMATIONS

As an example of the different calculations, we show in Fig. 1 the various total cross sections for leaving the ion

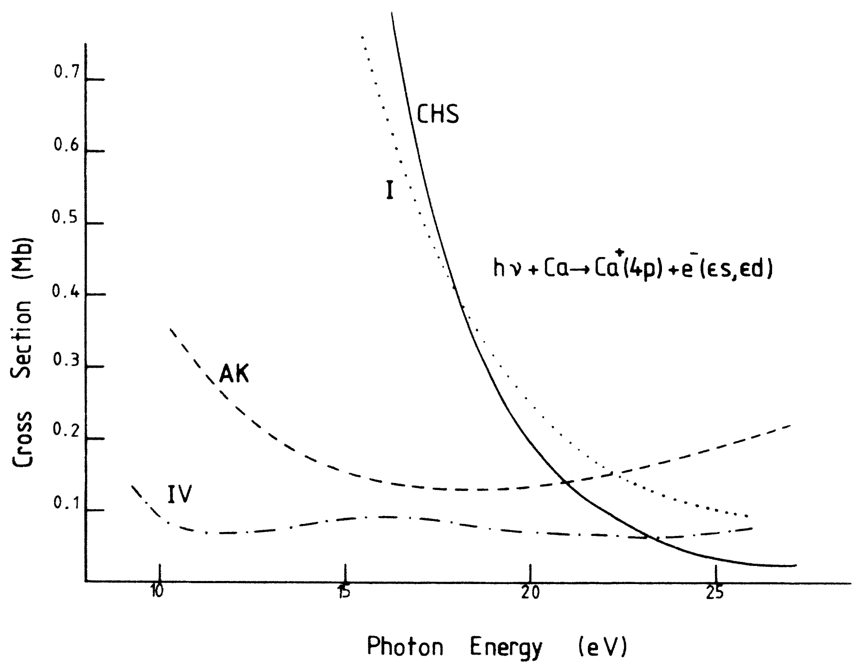

FIG. 1. Total $4p$ cross sections calculated in different approximations. Present work: I: simplified basis, no coupling between continua; IV: best basis with coupling between continua. CHS: Ref. 4; AK: Ref. 5.

in the $4p$ state. The figure shows the rather good agreement between the calculation due to Cowan *et al.*[4] (CHS) and calculation I. The effect of including full correlation (i.e., calculation III) is rather small in this case and cross section III (not shown) is located just below I. However, introduction of the coupling between the continua reduces the cross section dramatically (IV) and this curve is close to the result of calculation II, although the difference is a little larger than between I and III.

Thus we conclude that in this energy region full correlation is relatively unimportant for the $4p$ cross section but coupling between the continua is very important. Also the effect of virtual autoionization due to the $3p \rightarrow 3d$ excitation[4] is rather small in this energy region (on the $4p$ cross section). Altun and Kelly's[5] result (AK) is in between I and IV and is not reproduced by our approximations.

The situation for the $4s$ cross section is somewhat different. This cross section has a "Cooper minimum" which is absent in the HF approximation and the position of the minimum is critically dependent on the details of the calculation. Some of the calculations of the $4s\epsilon p$ cross section are shown in Fig. 2. In calculation I, the "Cooper minimum" is located at 12 eV but coupling the continua, II, moves the minimum down below the $4p$ threshold. Inclusion of full correlation also moves the minimum down, though not by so much (to 11 eV in calculation III, not shown). In Refs. 2 and 3 the minimum is found below the $4p$ threshold, at 8.2 eV in the MBPT calculation[2,5] and at 7.4 eV in the R-matrix calculation.[3] That the minimum in the R-matrix calculation is lower than in the MBPT calculation is consistent with the fact that the coupling between continua built on different thresholds was not included in the latter. As a consequence we find that our calculated $4s\epsilon p$ cross section (in IV) is larger at threshold than that published by Altun and Kelly.[5]

The position of the "Cooper minimum" in the R-matrix calculation is below the $3d$ threshold and this fact gives rise to changes in the shape of the Fano-type $3dnp$ resonances in the cross section. A recent measurement of the shape of the $3dnp$ resonances[13] has been interpreted as showing that the "Cooper minimum" must be located above the $3d$ threshold contrary to the R-matrix prediction. However, we believe that this conclusion may depend on the interpretation of the data since there appears to be good agreement between the calculated[3] and observed[13] spectrum except for the shape and position of an interloping resonance which was identified as $4p\,5s\ {}^1P$.

The somewhat unusual shape of the $4s\epsilon p$ cross section in Fig. 2 is due to a combination of two effects. The first (weak) maximum being the normal maximum following a "Cooper minimum" and the (onset to the) second being caused by virtual autoionization due to the $3p \rightarrow 3d$ excitation. The first maximum is only weakly present in the results due to Cowan *et al.*[4] perhaps because the "Cooper minimum" in that calculation is located slightly higher than in any of the other calculations.

Figure 2 shows that full correlation in this case is important (the difference between II and IV). However, the most important effect for this cross section is, as already emphasized in Ref. 4, the effect of the $3p \rightarrow 3d$ excitation. This can be seen by comparing curve I in Fig. 2 with Fig. 2 in Ref. 3 which differ by the inclusion of some $3p \rightarrow nl$ excitations in calculation I. Somewhat less important is the coupling between the continua (IV or II compared to I).

We conclude that the $4s\epsilon p$ cross section is strongly in-

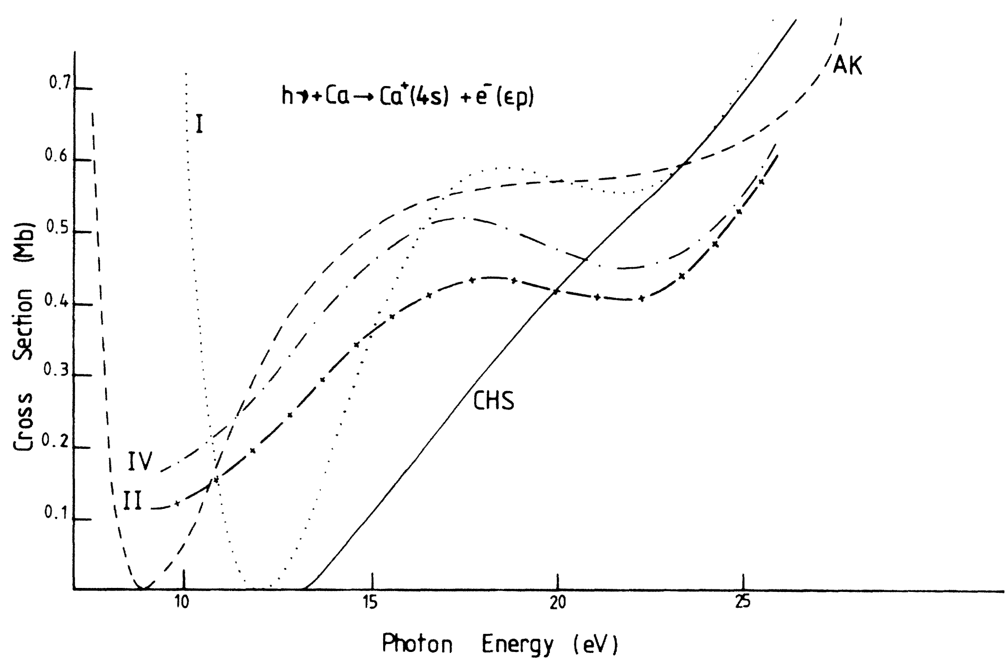

FIG. 2. $4s\epsilon p$ cross sections calculated in different approximations. Present work: I: simplified basis, no coupling between continua; II: simplified basis with coupling between continua; IV: best basis with coupling between continua. CHS: Ref. 4; AK: Ref. 5.

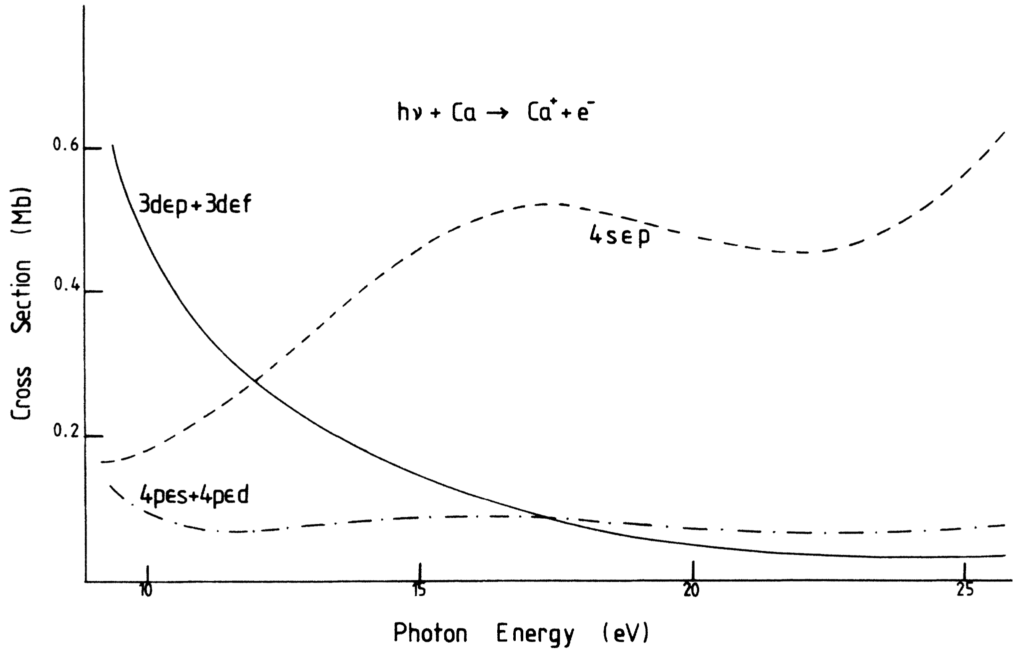

FIG. 3. Total $4s$, $3d$, and $4p$ cross sections as calculated in the present work (calculation IV).

fluenced by the virtual autoionization due to the $3p \rightarrow 3d$ excitation, and by the coupling between the continua. The inclusion of full correlation is less important although more important than for $4p$.

For the $3d$ cross section there is, as already mentioned, better agreement between the different results than for $4s$ or $4p$. This is because neither the effects of coupling the continua, full correlation or autoionization are as important as for the two other cross sections.

IV. RESULTS

Figure 3 shows the total cross sections for leaving the ion in the $4s$, $3d$, or $4p$ states from just above the $4p$ threshold at 9.25 eV to about 26 eV as obtained in calculation IV. The total cross sections for leaving the ion in either the $3d$ or $4p$ state are the sum of two partial cross sections as indicated on the figure. The ground state wave function is based on the diagonalization of a 97×97 matrix while the final ^1P state has 190 components. The theoretical thresholds have been adjusted to correspond to the observed positions. The shape of the $4s\epsilon p$ curve has been discussed above. Figure 3 shows that the $4p$ cross section has a weak maximum in the energy range where $4s\epsilon p$ has its secondary maximum. The former is presumably due to the strong coupling between the $4s$ and $4p$ continua in this region. This coupling has a spectacular consequence. In both previous calculations it was predicted that the $4p$ cross section would be larger than the $4s$

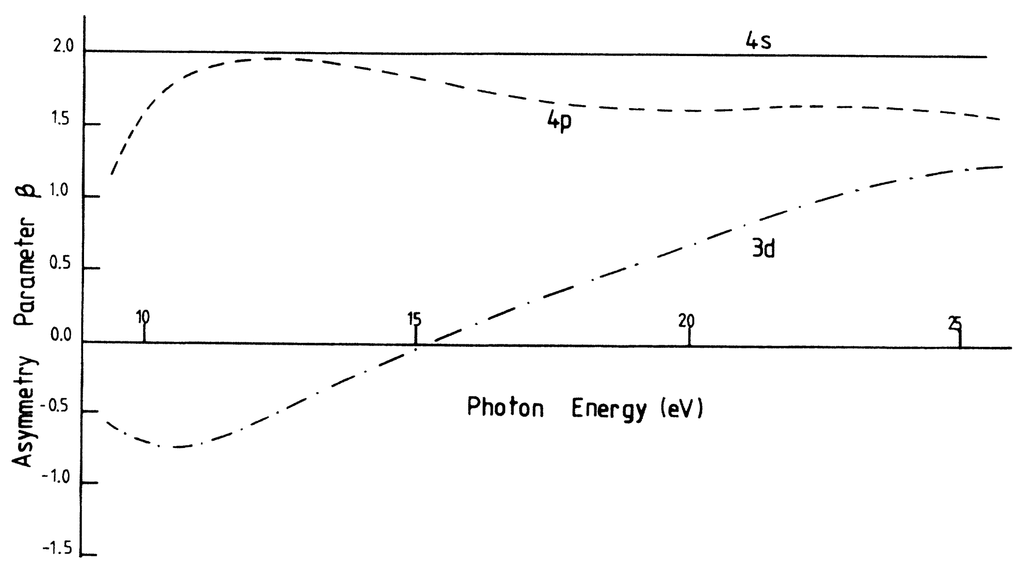

FIG. 4. Calculated β factors (calculation IV).

TABLE I. Cross sections and β factors at 21.22 eV. Calculated relative cross sections at 90° to the direction of the incident photon are compared to experimental values obtained by Süzer *et al.* (Ref. 9) The relative values are normalized to 100 for the 4*s* line. Also values derived from the calculations by Cowan *et al.* (Ref. 4) and Altun and Kelly (Ref. 5) are shown.

Photoelectron line	Q (Mb)	β	$Q(90°)$[a] (Mb)	Relative 4*s* at 90° Present[b]	CHS[b,c]	AK[b,d]	Expt.[e]
4*s*	0.4587	2.000	0.6881	100	100	100	100
3*d*	0.03917	0.852	0.04751	6.90	3.2	4.5	4.5
4*p*	0.06689	1.649	0.09447	13.7	20.7	24.0	10.3

[a] $Q(90°)=Q(1+\beta/4)$.
[b] The values at 90° are obtained using the β factors in column 3.
[c] Reference 4.
[d] Reference 5.
[e] Reference 9.

cross section in a region from the 4*p* threshold. The present calculation does not confirm this result. The 4*p* cross section is everywhere smaller than the 4*s* cross section. However, the 3*d* cross section is still predicted to be larger than the 4*s* cross section in the region from the 4*p* threshold (in fact from below this threshold) and up to approximately 12 eV. In judging the reliability of this result it should be remembered that post-collision effects, which are neglected here, might be important so close to threshold.

Figure 4 shows the calculated β factors in the same energy range. Since our calculation is nonrelativistic, the β factor for the 4*s* line is equal to two independently of the energy. The value for 4*p* is also fairly independent of energy, except close to threshold, and roughly equal to 1.6 while the value for 3*d* varies rather strongly with energy.

With the calculated β factors it is now possible to make a comparison with the measured satellite intensities at 21.22 eV. This comparison is shown in Table I. Also results obtained from the calculations by Cowan *et al.*[4] and by Altun and Kelly[5] using the β factors calculated in the present work are shown. For the 4*p* line our results are clearly in better agreement with observations than are the previous calculations while our value for 3*d* is somewhat larger than observed and slightly worse than that obtained in the previous calculations. No error limits are given for the experimental measurements and with this in mind we conclude that the *R*-matrix approach gives reasonable agreement with experiment (at 21.2 eV) with the present set of ionic basis states.

There are much larger differences between the different calculations below 21.2 eV and a comparison with experiment at lower energies would therefore be more significant.

V. CONCLUSIONS

We have presented nonrelativistic cross sections for photoionization with excitation of the 4*s* electrons in the ground state of the neutral Ca atom. A number of factors contribute to make the calculations very difficult close to threshold and we have shown that particularly the 4*s* and 4*p* cross sections are very sensitive to the effects of the $3p \rightarrow 3d$ resonance (this is true more than 15 eV below the resonance for the 4*s* cross section), to the coupling of the different continua and to correlation in the initial and final state. The latter was also noted by Altun and Kelly[5] as it resulted in extensive cancellation in their calculated cross sections. The difficulties involved can be appreciated from the fact that factor of 2 changes in the lowest order results can be called small when compared to the important ones. It would therefore be too optimistic to claim high accuracy for the present calculation although we believe it is more accurate than the previous ones.

We hope that this and the previous calculations on photoionization of Ca (and in particular the differences between them) will stimulate systematic measurements of these cross sections in the (photon) energy range below 20 eV.

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