

Photodetachment cross section for Ca^-

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Multiconfiguration Hartree-Fock calculations for photodetachment cross sections in Ca^- are reported, both to the ks^2S and kd^2D final state. Correlation is important to the binding of the $4s^24p^2P$ state and also to the cross section. In the final state, correlation is particularly important for the kd partial cross section. The value of the electron affinity in Ca^- is critical to agreement in the length and velocity form of the cross section. Better agreement is obtained when a theoretical value is used. Agreement with an experimental photodetachment cross section is good.

I. INTRODUCTION

Recently a bound state has been predicted [1,2] and observed [3] for the negative Ca ion. This atom was considered earlier [4] not to form a stable negative ion due to its closed shell structure and the stability of the negative Ca ion is exclusively due to correlation [1,2]. This makes this state rather unique and has led to considerable activity both experimentally as well as theoretically. From a comparison with Sc, the $4s^23d^2D$ state could be expected to be the ground state in Ca^- . However, the spatial extension of the $3d$ orbital just at the beginning of the transition elements is very sensitive to the environment and although the "collapse" of the $3d$ orbital is less spectacular than the collapse of the $4f$ orbital between Ba and La, it is still a noticeable effect [5] and it would lead to a weaker binding of the $3d$ orbital in Ca^- than expected on the basis of isoionic comparisons. On the other hand, Froese Fischer has found [2] that the unfilled $3d$ shell has a very important effect on the binding of the $4p$ electron in Ca^- and that in fact no bound Hartree-Fock (HF) orbital exists for Ca^- .

It is interesting to compare with the situation in Cl where the d series is important for the binding of the $3s3p^6^2S$ state [6,7] despite the small overlap between the $3p$ orbital and the (un-collapsed) $3d$ orbital. In this case the interaction with the d series, in particular, the continuum part [7], is instrumental in giving the lowest 2S state $3s3p^6$ character while in F the $2s2p^6^2S$ state has not been identified in the bound spectrum and is believed to lie in the continuum. Similarly Froese Fischer has shown [2] that the $3s^23p^2P$ state is not bound in Mg^- and ascribed this to the lack of an inner unfilled d shell.

Continuing the analogy, we would expect that the $4s^23d^2D$ state in Ca^- would be mixed into a number of states and that it could be difficult to identify among the possible metastable states of Ca^- . A number of predictions have been made of the position of the $4s^23d^2D$ shape resonance varying from 0.81 eV as reported by Kurtz and Jordan [8] to 2.28 eV reported by McCurdy,

Lauderdale, and Mowrey [9] while Amusia and Cherepkov [10] predicted 1.67 eV and Amusia *et al.* [11] gave a value of 1.25 eV. The large difference between the first two values is largely due to the fact that an empirical core-polarization potential was used by Kurtz and Jordan [9] but not by McCurdy, Lauderdale, and Mowrey [9], which gives an indication of the difficulties involved in *ab initio* calculations of this quantity.

It should be mentioned that already Amusia and Cherepkov [10] predicted that the $4s^24p^2P$ state should be located below $4s^23d^2D$ and that Johnston and Burrow [12] suggested that the reason that they did not observe a shape resonance associated with the $4s^24p^2P$ state could be that it was bound. The calculations by Kurtz and Jordan [8] as well as by McCurdy, Lauderdale, and Mowrey [9] predicted that 2P should be found below 2D and Kurtz and Jordan [8] proposed that the electron affinity of the 2P could be close to zero.

Before the identification of $4s^24p^2P$ as a bound state Kazakov and Kristoforov [13] measured differential cross sections for e -Ca scattering and interpreted them on the basis of $4s^23d^2D$ and $4s^44p^2P$ being metastable states giving rise to shape resonances. Recently, Yuan and Zhang [14] have calculated cross sections for electron scattering and interpreted the differential cross section on the basis of $4s^23d^2D$ being the only metastable state. In their calculation, they used a potential designed to include core-polarization effects but they did not include correlation in the continuum.

At the same time Johnston, Gallup, and Burrow [15] have reported in more detail their earlier measurements [12] of e -Ca scattering and identified two states at 1.1 ± 0.15 eV and 2.9 ± 0.15 eV as being due to the $4s^23d^2D$ shape resonance and the $4s4p^2^2D$ core excitation mixed roughly in the proportion 50:50 in such a way that the lower state (at 1.1 eV) has a very small dipole matrix element connecting it with the Ca^- ground state due to destructive interference while for the upper state the interference is constructive. This is roughly in agreement with the experimental detachment cross section

published by Heinicke *et al.* [16] that has a minimum around 1.2 eV and a pronounced maximum around 3 eV. However, the calculations of Johnston, Gallup, and Burrow [15] were made using analytic basis sets that can be difficult to guarantee completeness in a case such as the present one where the spatial extension of the $3d$ orbital depends strongly on the nature of the state [7]. Johnston, Gallup, and Burrow [15] did not publish a theoretical cross section and also for this reason, an independent calculation of the photodetachment cross section is useful.

A number of calculations concerning photodetachment cross sections has recently been published mainly concerning alkali and alkalilike atoms. Amusia and co-workers [17] have used the random-phase-approximation exchange approach for Na^- , Ag^- , I^- , and Si^- and have emphasized the importance of intrashell as well as inter-shell correlations for the photodetachment cross sections. The multiconfiguration Hartree-Fock (MCHF) wave function determined by Froese Fischer [2] for the Ca^- ground state on the other hand includes only intrashell correlation which makes it interesting to determine the quality of the cross sections which can be obtained from it.

Recently Chernysheva *et al.* [18] have proposed a new method based on the Dyson equation to calculate the properties of negative ions and Johnson, Sapirstein, and Blundell [19] have obtained good results for the electron affinity of Ca^- , Sr^- , and Pd^- using this technique. Gri-bakin *et al.* [20] have presented photodetachment cross sections for the Ca^- , Sr^- , and Ba^- ground states with the ground-state wave functions obtained using this technique and HF wave functions for the photoelectrons. The results show a large difference between length and velocity formulations. As far as we know this is the only published theoretical photodetachment cross section for Ca^- but the restriction to a HF final state means that it is interesting to compare with the result of the MCHF approach for which this restriction can be removed.

The experimental photodetachment cross section determined by Heinicke *et al.* [16] was published before it was known that Ca^- has a stable ground state. We assume here that this state is the main component of the Ca^- beam they studied but we note that the content of the beam is unknown except that the ions had a lifetime longer than 10^{-5} sec and a metastable component in the beam cannot be ruled out. However, it has been argued [21] by other workers that the beam was in the Ca^- ground state.

II. DESCRIPTION OF THE CALCULATIONS

The wave functions for the initial state were those reported earlier [2]. In order to check the sensitivity of the cross section to the accuracy of the initial-state wave function, calculations were performed for both expansions (b) and (c): the former contains all possible configuration states whose orbitals are from the set $\{4s, 5s, 4p, 5p, 3d, 4d, 4f\}$ whereas the orbital set for the latter was $\{4s, 5s, 6s, 4p, 5p, 6p, 3d, 4d, 5d, 4f, 5f, 5g\}$. Core orbitals for the final state were selected to be those of the

initial state. This assumption is important in the evaluation of the matrix element for the cross section.

A. Calculations for $4s^2ks^2S$

The first calculation was a simple Hartree-Fock calculation for the final state using expansion (b) for the initial state. The target $4s^2^1S$ state was a fixed core Hartree-Fock calculation. The photon energy (in Ry) was expressed as the sum of the binding energy of the $4p$ electron in Ca^- plus the energy of the continuum electron; the observed binding energy [3] of 0.000316 Ry was used in the evaluation of the expression for the cross section. The results are shown in Fig. 1(a). Note the lack of agreement in length and velocity forms at both small and larger values of the electron energy.

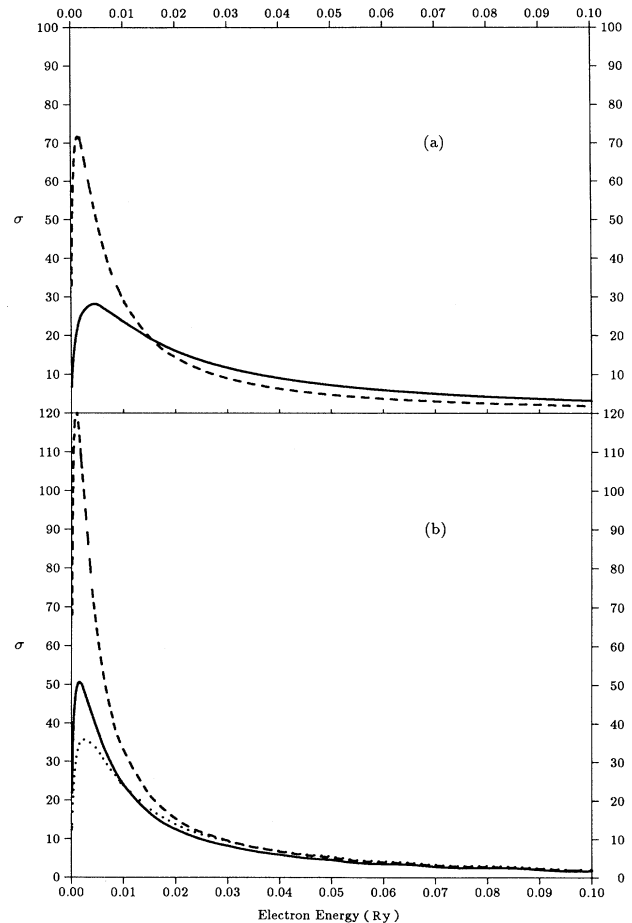


FIG. 1. Photodetachment cross section (in Mb) for $\text{Ca}^- 2P - ks^2S$ for different wave functions and experimental binding energy (solid curve: length form; dashed curve: velocity form). (a) Moderately accurate initial state and fixed core Hartree-Fock final state. (b) Accurate initial state and correlated final state (dotted line is length form for moderately accurate initial state).

A second set of calculations was performed using a multiconfiguration expansion over the configuration states $\{4s^2, 4p_1^2, 3d_1^2\} ({}^1S)$ for the target state along with the following expansion for perturbers:

$$4s\{4p_2^2, 4p_2 5p_2, 3d_2^2, 3d_2 4d_2, 5s_2^2, 5s_2 6s_2\} ({}^1S), 3d_3 4p_3^2.$$

The continuum function ks_1 was required to be orthogonal to $4s$, but not to $5s_2$. (The subscripts refer to different orthogonal sets with all orbitals orthogonal to $4s$.) The orbitals, $4p_2, 3d_2, 5s_2$ were determined from fixed core, average energy Hartree-Fock calculations for $4s4p_2$, $4s3d_2$ and $4s5s_2$, respectively; the $3d_3$ and $4p_3$ orbitals from an average energy Hartree-Fock calculation for $3d_3 4p_3$. With these orbitals fixed, MCHF calculations were performed in which orbitals $5p_2, 4d_2, 6s_2, 3d_3$ were varied and the continuum orbital determined along with the mixing coefficients in the expansion. The results

using expansion (c) for the initial state are given in Fig. 1(b). Note the excellent agreement in the length and velocity forms away from threshold. We show also the result for the length form based on expansion (b) for which the discrepancy near threshold is somewhat larger. At threshold, the cross section is sensitive to the binding energy. In the length form, the factor (binding energy plus electron energy) occurs in the numerator of the expression for the cross section whereas in the velocity form it occurs in the denominator. An error in the binding energy is relatively unimportant away from threshold but, because the binding energy for the negative ion is so small, an error in the binding energy is critical. In Fig. 2(a) the cross section based on the use of the theoretically predicted value of 0.005 12 Ry [2] is shown. Note the dramatic improvement in the agreement between the two forms. Figure 2(b) shows that a similar redefinition of the binding energy does not bring the Hartree-Fock length and velocity cross sections into agreement over the range of energy considered. Thus correlation is important in both the initial and final states.

B. Calculations for $4s^2 kd^2 D$

As in the previous case, the first calculation is a fixed core Hartree-Fock calculation, however, using expansion (c) for the initial state. The resulting cross sections are presented in Fig. 3(a) computed using the theoretical

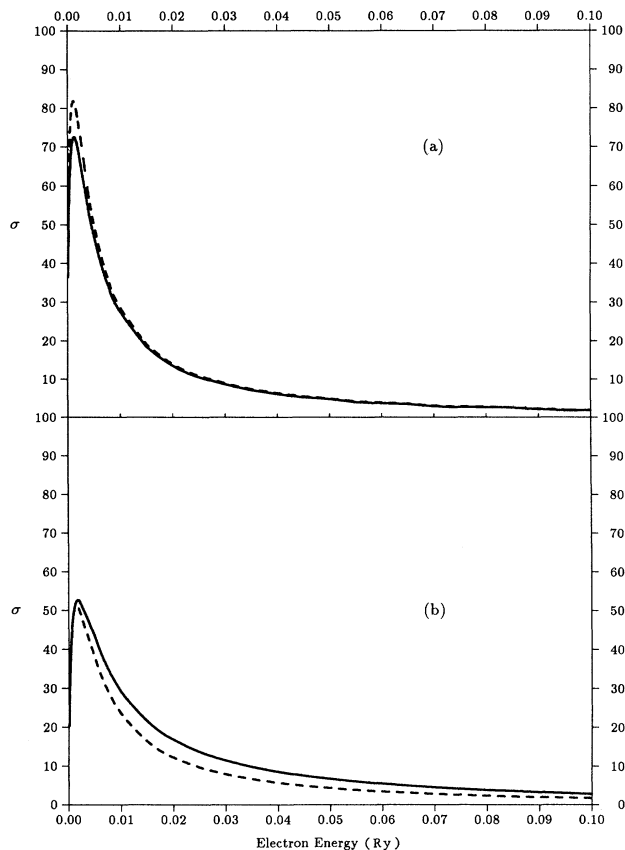


FIG. 2. Photodetachment cross section (in Mb) for $\text{Ca}^- 2P - ks^2 S$ for different wave functions and theoretical binding energy (solid curve: length form; dashed curve: velocity form). (a) Accurate initial state and correlated final state. (b) Accurate initial state and fixed core Hartree-Fock final state.

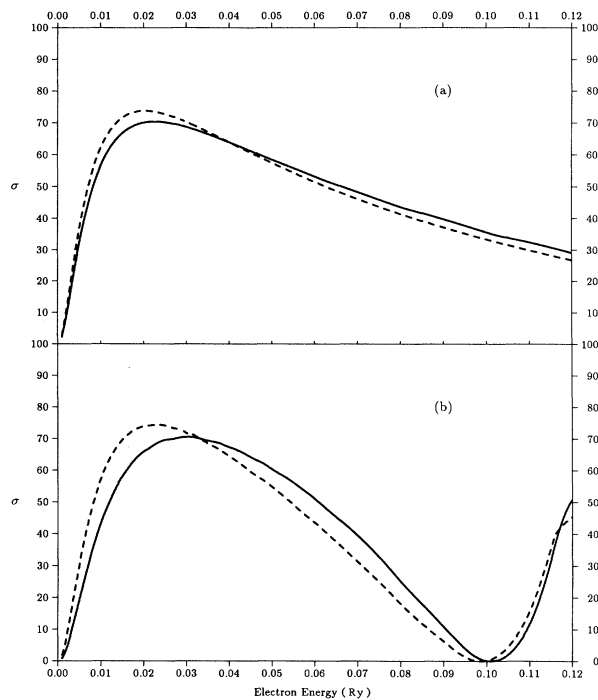


FIG. 3. Photodetachment cross section (in Mb for $\text{Ca}^- 2P - kd^2 D$ for different wave functions and theoretical binding energy (solid curve: length form; dashed curve: velocity form). (a) Accurate initial state and Hartree-Fock final state. (b) Moderately accurate initial state and correlated perturber in the final state.

binding energy. Agreement in length and velocity form is fairly good. However, earlier studies of transition probabilities [22] for the Ga I $4s^2 4p - 4s^2 nd$ Rydberg series have shown the importance of the $4s 4p^2 {}^2D$ perturber to the oscillator strengths. In fact, the transition matrix element between the states exhibits cancellation with the contribution from the $4s^2 4p - 4s^2 nd$ component having the opposite sign to that from $4s^2 4p - 4s 4p^2$.

The approach used for the $ks {}^2S$ case, where the interaction with the $4s 4p^2$ perturber is not large in the energy range under consideration, was not adequate for the

$kd {}^2D$ case: greater attention needed to be given to the representation of the perturber. At the same time, the earlier studies suggested that the $3d_1^2 {}^1S$ component to the representation of the target was not important. In order that the kd_1 orbital not be constrained by any orthogonality requirement, this component was removed from the representation of the target.

Fixed core MCHF calculations were performed for the $\{4s_1^2, 4p_1^2\} ({}^1S)$ target state. Fixed core MCHF calculations were then performed for the perturber state, expressed as an expansion over the configuration states

$$4s_2 \{4p_2^2, 4p_2 5p_2, 3d_2^2, 4p_2 4f_2, 5p_2 4f_2\}, 5s_2 \{4p_2^2, 4p_2 5p_2, 3d_2^2, 5s_2 5p^2\}, \\ \{4p_3^3, 4p_1 5p_1\}, 4d_3, 4s_1 \{5s_1 3d_2, 5s_1 4d_2, 3d_2 4d_2\}, 4d_3^3, 4p_3 4d_3 4f_3.$$

These configuration states were selected from a larger expansion in which configuration states with mixing coefficients less than 0.02 were deleted. Orbitals with a subscript of 1 needed to be introduced in order

to satisfy the constraints imposed by the limited non-orthogonal evaluation of matrix elements of the Hamiltonian with $\{4s_1^2, 4p_1^2\} kd_1 {}^2D$ configuration state [23]. Calculations were then performed varying the $5s_1, 5p_1, 5s_2, 5p_2, 4d_2, 4f_2, 4d_3, 4f_3$ orbitals while also determining the continuum orbital and mixing coefficients. The cross sections from these wave functions for the final state and expansion (b) for the initial state are presented in Fig. 3(b) and clearly depict the cancellation arising from the perturber. In this calculation, the energy of the target was that obtained from the two configuration MCHF calculation, namely, -676.78502 a.u.

The earlier study of lifetimes of the nd series of Ga I had shown the importance of an accurate position for the perturber [22]. In the present continuum calculations, the energy in the continuum is relative to that of the target and is specified as input data. In Fig. 4(a), results similar to those of Fig. 3(b) are presented, obtained from calculations in which the target energy was set to the best value of -676.78711 a.u. reported earlier [2]. This now has shifted the "Cooper minimum," where the transition matrix element has become zero, to a slightly higher electron energy. Finally, cross section calculations were performed for expansion (c) of the initial state and the same final-state functions. The results are displayed in Fig. 4(b). There is a marked improvement near threshold in the agreement between length and velocity forms and the agreement after the Cooper minimum is excellent. All the above calculations were performed using the MCHF atomic structure package (MCHF-ASP) [24] for bound states and its extension to continuum states [25].

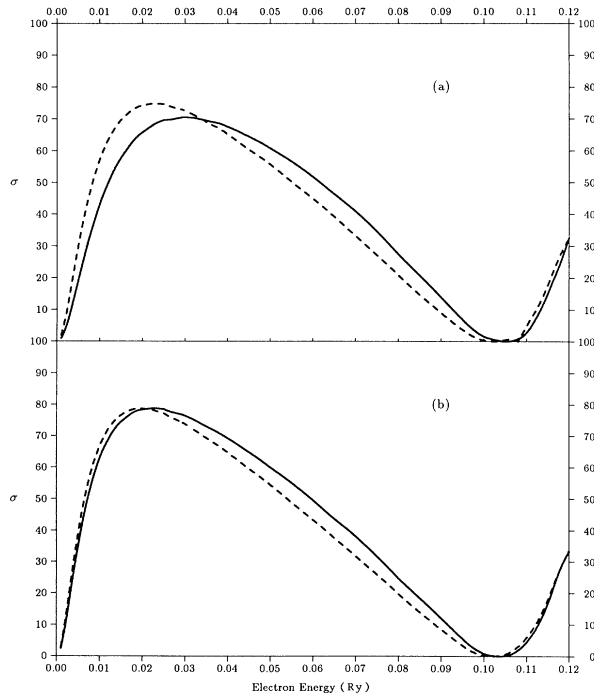


FIG. 4. Photodetachment cross section (in Mb) for $Ca^{-2}P - kd {}^2D$ in which the final-state wave function includes the perturber but the energy of the target is shifted to a more accurate value, calculated using a theoretical binding energy (solid curve: length form; dashed curve: velocity form). (a) Moderately accurate initial state. (b) Accurate initial state.

III. DISCUSSION OF RESULTS

Unlike the $ks {}^2S$ final state where the interaction with perturbers is small, the interaction with the perturber is crucial to the accurate prediction of the $kd {}^2D$ partial cross section. The latter differs significantly from the

cross section predicted by a Hartree-Fock final-state wave function in the energy range up to about 1.5 eV photon energy. An accurate description of the target appears not to be important provided the energy of the target used to determine the position in the continuum, namely,

$$E = E(\text{target}) + k^2/2$$

(in a.u.) is accurate. In both cases, improvement in the agreement between length and velocity forms was observed as more accurate wave functions were used in the description of the initial state.

Comparing the calculated cross section to the experimental one [16] in the common energy range 0.45–1.6 eV, we first note that the ks wave to a good approximation can be neglected except at the minimum in the kd cross section close to 1.4 eV. Comparing the calculated kd cross section with experiment there is quite good agreement: with a continuous decrease in the calculated cross section from 0.45 eV to a minimum close to 1.4 eV compared to the observed [16] minimum around 1.2 eV. The minimum in the theoretical cross section is caused by interference between the different parts of the final-state wave function in agreement with the observation of Johnston, Gallup, and Burrow [15]. Comparing with the calculation by Gribakin *et al.* [20] we note that they have used a HF wave function for the outgoing electron and their results should therefore be compared to our results with a HF continuum wave. There are reasonable agreements between the two sets of results, with the ks decreasing much faster than the kd contribution. However, the agreement between length and velocity forms is better in our case even for the HF continuum function and the minimum in the kd cross section is missing in their result since it is due to correlation in the continuum.

It is interesting that the agreement with observation appears to be so good for a calculation which does not include polarization of the $3s$ and in particular the $3p$ shell since it is known that core polarization is important for bound-bound transitions in Ca I (Refs. [26, 27]) as well as Ca II (Ref. [28]). On the other hand, Johnson, Sapirstein, and Blundell [19] note that the contribution to the

second-order self-energy in the Dyson equation from the $n=3$ shells in Ca^- is only 10% of the $4s$ contribution and Gribakin *et al.* [20] did not include the contribution from the inner shells at all. This is consistent with the fact that the pickup of an additional electron in Ca^- leads to an expansion of the valence shell since this could be expected to lead to a reduction in the importance of the polarization of the inner shells. This argument has been used [2] to suggest that the additional core-polarization effect on the total energy due to the $4p$ electron in Ca^- is compensated by a decrease in the core polarization associated with the $4s$ shell. However, while this argument can be justified for the energy it is less obvious for the cross section and it seems more likely that the weak influence of core polarization is due to the fact that the photon energy is too small to excite, even virtually, the inner shells as found, for example [17], for Na^- . We noticed that the calculation of the kd^2D cross section above 1.5 eV became more difficult, which perhaps can be related to the neglect of core polarization in our approach.

Clearly evident in this work is the marked improvement in the ks^2S and kd^2D partial cross sections when a theoretical binding energy is used in the computation. The value of 0.005 12 Ry used in this paper is in reasonable agreement with a value of 0.004 16 Ry reported by Johnson, Sapirstein, and Blundell [19], and 0.005 15 by Kim and Green [29]. Agreement between length and velocity forms is a necessary condition for accurate wave functions but is not a sufficient condition to prove the correctness of the theoretical binding energy. It is well known from the computation of f values for bound-bound transitions that the agreement between length and velocity formulations in some cases can be much better with an (incorrect) theoretical transition energy than using the (correct) experimental transition energy. Thus it is difficult to say whether the better agreement between length and velocity using the theoretical energy has any physical significance.

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