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Photoelectron spectrum of Ca between 11 and 28 eV

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We present a calculation of the photon energy dependence of the photoelectron spectrum of Ca from 11 to 28 eV, roughly the region between the $4p$ threshold and the lowest resonance due to $3p \rightarrow 3d$ excitations. Because of the occurrence of a "Cooper minimum" for $4s \rightarrow \epsilon p$ excitation close to threshold, which is not reproduced for the satellites, we predict that at low photon energy the $3d$ and particularly the $4p$ satellite will be stronger than the main $4s$ line.

The study of photoionization has provided important information about correlation effects in atoms. In the alkaline earths, in particular, the importance of double excitations in the outer ns^2 shell is well established, and has been studied for Ca both experimentally[1] and theoretically[2,3] in the photoabsorption spectrum below the $4s^2 \rightarrow 3d\epsilon l$ and $4s^2 \rightarrow 4p\epsilon l$ ionization thresholds.

Correlation effects can also be studied in the photoelectron spectrum for photon energies above the $4s^2 \rightarrow 4p\epsilon l$ ionization threshold. This is a region that is not well suited for photoabsorption experiments because only weak resonance structures are expected until inner-shell excitations become energetically possible. However, the so-called satellites in photoelectron spectra, which can be observed in this region of photon energies, are due to correlation in the initial or the final state or both. Experimentally it is now becoming possible by use of synchrotron radiation to study in detail the satellite spectra as a function of photon energy, while previously measurements at only a few fixed energies were possible. This new possibility has already led to some surprising results in the rare gases[4,5] and many similar systematic studies can be expected in the near future.

In recent experiments on Xe it was found[4] that satellites in the energy region of the "Cooper minimum" for $5s \rightarrow \epsilon p$ ionization become much stronger than the main $5s$ line. However, it has been shown recently[6,7] that the strength of this satellite spectrum is due to $5p$ satellites which overlap the $5s$ satellites and are stronger than these at the "Cooper minimum" for $5s \rightarrow \epsilon p$ ionization.[7] Since the $5s$ satellites correspond to correlation in the final ionic state, the "Cooper minimum" for the main line is to first order reproduced in the satellite cross sections.[6] This is essentially because both satellites and main line depend on a $5s \rightarrow \epsilon p$ dipole matrix element, which has a fairly weak energy dependence over the energy range that covers main line and satellites.[6]

In this paper we predict that a similar experiment performed in the region of the "Cooper minimum" for $4s^2 \rightarrow 4s\epsilon p$ ionization in Ca might lead to $4s$ satellites that are genuinely stronger than the main $4s$ line. This possibility arises because the satellites in Ca are due to correlation in the initial state, which means that they depend on different dipole matrix elements than the main line; thus, their energy dependence can be entirely different.

Very little theoretical work has been done on photoionization with accompanying excitation,[8] but conceptually it is easy to understand. The configuration interaction (CI) in the Ca ground state between $4s^2$ and $4p^2$, say, mixes part of the latter basis function into the ground state, and ionization from this part of the ground-state wave function leaves the Ca ion in the excited $4p$ state. It is obvious that there is a relation between the amount of $4p^2$ basis function in the ground-state wave function and the probability for leaving the ion in the $4p$ state.

Süzer, Lee, and Shirley[9] proposed that the probability depends *only* on the amount of $4p^2$ basis function, and that consequently measurements of the satellite strengths in photoelectron spectra could be used to determine experimentally the ground-state composition. This proposal was based on good agreement between the observed (relative) $4p$ satellite intensity at 21.2-eV photon energy and multiconfiguration Hartree-Fock (MCHF) calculations by Kim and Bagus[10] of the ground-state composition. However, for the $3d$ satellite intensity a discrepancy of a factor of 10 was observed, as shown in Table I (column 4). The discrepancy

TABLE I. Calculated and observed relative satellite intensities in Ca at 21.2-eV photon energy.

Final ionic state	Energy of photoelectron (eV)	Observed relative intensities	Ground-state composition		Calculations	
			MCHF[a,b]	CI[a,c]	A[a,d]	B[a,e]
$4s$	15.10	100	100	100	100	100
$4p$	11.97	10.3	8.7	7.8	428	22
$3d$	13.41	4.5	0.34	0.45	82	4

[a]Renormalized to 100 for $4s$.
[b]Reference 10.
[c]Ground state used in this work.
[d]Dipole matrix elements included together with correlation in the initial but not in the final state.
[e]Dipole matrix elements and correlation in the initial and the final state included.

was confirmed for Ca as well as for the other alkaline earths by more elaborate MCHF calculations by Hansen,[11] who proposed that the discrepancy was due to the neglect of the dipole transition matrix elements which destroy the direct proportionality of photoelectron intensities to ground-state composition. This proposal is tested here and found to be only a small part of the truth. Of equal importance is final-total-state CI, particularly that associated with resonances arising from inner-shell excitation followed by autoionization.

We here report the first explicit calculations of the $4p$ and $3d$ satellite strengths. The calculations were carried out using the chain of computer programs developed by Cowan,[12] in which each continuum is represented by a sequence of pseudodiscrete segments. Since the energy grid we use is too coarse to give a satisfactory description of the strong $3p \rightarrow nd$ resonances, our results cover only the energy region up to the $3p^64s^2 \rightarrow 3p^54s^23d\,^1P$ resonance (31.5 eV).[13]

We started by considering only initial-state CI, making calculations that used a ground-state wave-function expansion $4s^2+4p^2+3d^2+5s^2+5p^2+4d^2$ (only the first three components have a significant size: Table I, column 5), and that included the $4s \rightarrow \epsilon p, 4p \rightarrow \epsilon s$, ϵd, and $3d \rightarrow \epsilon p, \epsilon f$ dipole matrix elements in the length formulation. HF calculations were used to determine the basis functions, but a correlation correction was added to the diagonal energies as described in Ref. 12. These calculations led to the predictions in Table I (calculation A, column 6), which show that at 21.2 eV the presumed improvement in the calculation leads to violent disagreement with experiment. The reason is that the $4p \rightarrow \epsilon d$ and $3d \rightarrow \epsilon f$ dipole matrix elements are much larger than the $4s \rightarrow \epsilon p$ one at this energy.

Consequently, final-total-state CI effects were considered in order to explain the observed satellite strengths. Firstly, we considered the possibility of interaction *between* the different continua $4s\epsilon p$, $4p\epsilon l$, and $3d\epsilon l$, which might lead to a redistribution of the calculated satellite strengths. This effect was judged to be negligible in this energy range by Süzer *et al.*[9] and we have made calculations that confirm this judgment.

Secondly, we considered the effect of inner-shell excitations followed by autoionization. The $3p \rightarrow 3d$ excitation can be expected to be very strong and $3p^54s^2nd$ states can autoionize to $3p^64s\epsilon p$ but not to $3p^64p\epsilon l$. Although even the lowest $3p^64s^2 \rightarrow 3p^54s^2nd\,^1P$ resonance is 10 eV above the photon energy of interest, the strengths of the $3p^64s^2 \rightarrow 3p^54s^2nd$ transitions are so much larger than the direct transition to the continuum, and the $3p^54s^2nd$-$3p^64s\epsilon p$ CI is so strong, that the virtual process turns out to greatly influence the total $4s^2 \rightarrow 4s\epsilon p$ cross section (i.e, the intensity of the main photoelectron line). In contrast with this, the direct $4p^2 \rightarrow 4p\epsilon l$ and $3d^2 \rightarrow 3d\epsilon l$ transitions are inherently very strong (cf. column 6 with column 5 of Table I), so that effects of the $3p^54p^2nd$ and $3p^53d^2nd$ autoionizing levels on satellite-line intensities are comparitively unimportant.

Thirdly, it is known that the interaction between the $3dnp$ and the $4snp/\epsilon p$ series leads to a considerable reorganization of both series.[14] Although it was not obvious that this reorganization would be of importance far into the continuum, it was found in both Refs. 2 and 3 that the "Cooper minimum" for $4s$ ionization is displaced towards lower energies by the influence of the double excitations in the $4s^2$ shell. Consequently, we found it necessary to include the $3dnp$ resonances in the determination of the $4s\epsilon p$ cross section.

Transition probabilities were calculated for ionization to $3p^64s\epsilon p$, $4p\epsilon l$, and $3d\epsilon l$ states taking into account $3p \rightarrow nd/\epsilon d$ excitations, part of the $3p \rightarrow 4s$ excitations, and also the effect of the $3p^63dnp$ series on the $4s\epsilon p$ cross section. This meant including the $3p^54s^2nd$, $3p^54p^2nd$, $3p^53d^3$, $3p^54s3d^2$, and $3p^63dnp$ configurations and the interactions among these configurations, as well as the interaction between them and the continua mentioned above. The interactions *between* the continua were neglected because their effects were found to be negligible in the calculation mentioned already. Whether or not this result will be correct in reality is not certain because of the reorganization of the $4s\epsilon p$ series induced by the $3dnp$ series. On the other hand, the admixtures of autoionizing states seem too small to induce mixing between the continua.

The HF calculations for the continuum states were made for the ^1P symmetry. [The $4s\epsilon p$ cross section is considerably different when calculated using HF (^1P) and HF(E_{av}) wave functions.] For most bound configurations we used HF(E_{av}) wave functions for the following reason. There is a strong LS-term dependence in HF calculations for $3p^53d$ configurations, particularly when the $3d$ orbital is on the verge of collapse;[15] however, this effect is automatically included when HF(E_{av}) wave functions are used for the $3p^54l^2d$ configurations and the series interactions explicitly included in a CI calculation with a sufficient number of $nd/\epsilon d$ configurations.[12,16] We used 5 bound and 15 continuum $3p^54s^2d$ configurations plus 4 $3p^54p^2d$ configurations for the $4s\epsilon p$ calculation, and 4 bound and 4 continuum $3p^54p^2d$ configurations for the $4p\epsilon l$ and $3d\epsilon l$ calculations.

In the present case the effect of including the autoionizing states (and hence resonance contributions to photoionization) is to increase the strength of the main line by a factor of 13 at 21.2 eV. A considerable part of the increase is due to the excitations to higher d configurations. The effect of the $3dnp$ series is also considerable even at 21.2 eV, but only when the autoionizing configurations are included. Also, the $3p^54s3d^2$ configuration can autoionize to $4s\epsilon p$, and was included.

A calculation of the $4s\epsilon p$ cross section including the effect of the lowest 6 bound $3p^54s^2nd$ configurations has been published by Altun, Carter, and Kelly.[2] The main interest in Ref. 2 was in the energy region below the $4p$ threshold and in the region of the $3p \rightarrow d$ resonances. Nevertheless, the increase in the cross section relative to the HF value can be seen from Fig. 5 of Ref. 2, although the amount of increase is difficult to judge on the scale used in that figure. In both Refs. 2 and 3 it is found that the "Cooper minimum" for $4s \rightarrow \epsilon p$ ionization is moved towards lower energy when correlation is included. We find the same effect, although not as pronounced. This is apparently because we have included fewer double excitations in the $4s^2$ shell than is the case in Refs. 2 and 3. How large an effect this neglect will have *above* the "Cooper minimum" is difficult to guess, but there are indications from comparison with experiment that our $4s\epsilon p$ cross section should be displaced towards lower energies.

For the $4p\epsilon l$ and $3d\epsilon l$ cross sections above the $4p$ threshold, no published values exist. The main part of the effect of autoionization on the $4p$ satellite intensity is due to the equivalent $3p \rightarrow nd$ excitations with $3p^54p^2nd$ as intermediate states. The overall effect is a *decrease* in intensity in the energy region studied. The magnitude of the decrease is about 30% at 21.2 eV, which should be compared to the factor of 13 *increase* found for the main $4s$ line at the same energy.

For the $3d$ satellite a *decrease* of the same size as for $4p$ is found when the autoionizing configurations $3p^5 3d^3$, $3p^5 4s^2 3d$, $3p^5 4p^2 3d$, and $3p^5 4s 3d^2$ are taken into account.

The final results at 21.2 eV are shown in Table I (calculation *B*, column 7). Compared with the experimental values of Süzer *et al.*,[9] the calculated $3d$ satellite intensity is now in good agreement with experiment. On the other hand, the $4p$ intensity is a factor of 2 wrong. However, it may be significant that the experiment was done at 90°, since the β factors for the different satellites are expected to be different; measurements at the magic angle are therefore necessary to check whether or not the disagreement is real. In addition, the $4s$ and $4p$ intensities are varying rapidly at 21.2 eV, and a change of a factor of 2 in the ratio is possible without large changes in the calculation. This can be seen from Fig. 1, which shows the energy dependence of the $4s\epsilon p$, $4p\epsilon l$, and $3d\epsilon l$ cross sections on an absolute scale both with and without inclusion of final-state CI. Owing to the "Cooper minimum" for $4s \rightarrow \epsilon p$ ionization, it can be seen that the $4p$ satellite is predicted to be stronger than the main line over a fairly large energy interval below 18 eV. If the $4s \rightarrow \epsilon p$ "Cooper minimum" is located at lower energy as found in Refs. 2 and 3, the energy region where the $4p$ satellite will be stronger than the main line might be pushed towards lower energies, which can improve the agreement with experiment at 21.2 eV.

We have not considered the region close to the $3d$ and $4p$ thresholds because the energy grid we use is too coarse to give a satisfactory description of this region. However, Scott, Kingston, and Hibbert[3] predict (Fig. 8 in Ref. 3) that the $3d\epsilon l$ cross section is larger than the $4s\epsilon p$ cross section *between* the $3d$ and $4p$ thresholds (7.8–9.2 eV), although they do not discuss the consequences of this result for the photoelectron spectrum. Similarly, Altun has calculated[17] that the $4p\epsilon l$ cross section at threshold is larger than that for $4s\epsilon p$. Both results agree with our prediction that the $3d$ and $4p$ satellites close to the $4p$ threshold will be stronger than the main line.

In conclusion, we predict that there is a pronounced energy dependence of the photoelectron spectrum of Ca below the $3p \rightarrow nd$ resonances, leading to the result that the satellites somewhere below photon energies of 18 eV for $4p$ and 14 eV for $3d$ become stronger than the main line. New measurements at the magic angle are necessary to verify this prediction.

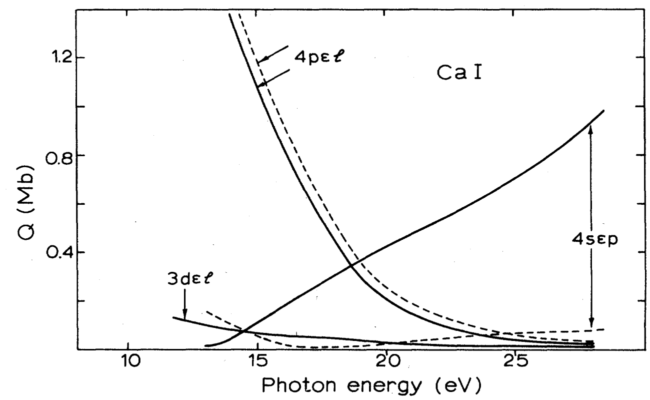

FIG. 1. The $4s\epsilon p$, $4p\epsilon l$, and $3d\epsilon l$ cross sections between 11 and 28 eV in Ca (summed over the two possible values of l). The dashed curve includes correlation in the initial but not in the final state. The fully drawn curve includes correlation in both the initial and the final state. For $3d\epsilon l$ only the fully drawn curve is shown since the difference between the two is very small on the scale used. The increase with energy of the solid $4s\epsilon p$ curve represents primarily the low-energy tail of the very strong and broad Beutler-Fano resonance arising from $3p^6 4s^2\,{}^1S_0$-$3p^5 4s^2 3d\,{}^1P_1$ excitation followed by autoionization. The center of this resonance is outside the figure at 31.5 eV.

Since resonance structures might change drastically the relative satellite strengths close to threshold, it is necessary to make measurements over a range of photon energies in order to arrive at an unambiguous result. Resonance structure has already been predicted in the $3d\epsilon l$ cross section between the $3d$ and $4p$ thresholds by Scott *et al.*,[3] and the observation of these at very low energy form a particular challenge to the experimentalist. However, our results show that very interesting results might be obtained also at somewhat higher energies.

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