Calculation of the dipole-allowed excitations of the $3p^4 4s4p$ and $3p^4 3d4p$ configurations in argon

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The energy spectrum of the argon $3p^4 4s4p$ and $3p^4 3d4p$ configurations with a total $J=1$ was calculated within the single-configuration relaxed-core Hartree-Fock approximation. The spin-orbit interaction was included in the calculation. The results indicate strong mixing of the ^1P terms which are the ones allowed to couple to the ground state via electric-dipole excitation. Most experimental lines could be identified using this calculation. The calculated spin-orbit splittings within groups of levels are in very good agreement with experiment. However, differences of the order of 1 eV between experiment and theory were found for the absolute positions of groups of levels. [S1050-2947(99)03702-6]

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Autoionizing resonances that involve the simultaneous excitation of two electrons provide very useful information about the effect of electron-electron correlation in the photoionization dynamics of atoms. Argon, with an initial closed shell, is a very convenient system for such studies. Experimental results for the absorption in the region of the $3p^4 n\ell n'\ell'$ autoionizing resonances have been available for some time now [1]. In that work Madden, Ederer, and Codling [1] presented a detailed analysis for the photon excited $3s \rightarrow np$ and the $3p^6 \rightarrow 3p^4 n\ell n'\ell'$ transitions. They found five resonances belonging to the $4s4p$ configuration and 14 of the $3d4p$ multiplet. All the observed states result from direct dipole excitation from a ^1S ground state and thus have $J=1$. If one considers the LS composition of these states, one would expect them to have a significant component of ^1P terms mixed in. More recently Baig and Ohno [2] presented independent absorption data for the $3s \rightarrow np$ single electron excitations, and also results of nonrelativistic Hartree-Fock (HF) and relativistic Hartree-Fock calculations. In their calculation [2] they found that the experimental energies of the $3s \rightarrow np$ resonances were about 4 eV lower than the HF values obtained from the difference between the calculated ground state energy and the calculated excited energy. They indicate that this shift is due to the interaction with the $3p^4 4snp$ and $3p^4 3dnp$ configurations. They also discussed the effect of a two electron $4s4p$ resonance near the $10p$ member of the series, and calculated, within a relativistic HF scheme, the position and term composition of all 14 $4s4p$ states with total angular momentum $J=1$. Of these states only four were found with more than 10% ^1P character, one less than the number of resonances observed by Madden, Ederer, and Codling [1]. However, Baig and Ohno [2] made no attempt to match the calculated levels with the observed resonances. More experimental information was obtained in a recent, high-resolution, photoelectron measurement [3], where another window resonance was found at 28.875 eV between the $8p$ and $9p$ members of the $3s \rightarrow np$ series. So far, there are no other theoretical calculations of the $3d4p$ and $4s4p$ configuration splittings.

The present article presents a nonrelativistic, single-configuration HF calculation of the $3p^4 4s4p$ and $3p^4 3d4p$ resonances, in which the effect of spin-orbit interaction is included. The levels with more than 1% contribution from ^1P terms were identified and their calculated positions were compared with the calculation of Baig and Ohno [2], and with the experimental results of Madden, Ederer, and Codling [1], and of Caldwell, Krause, and Whitfield [3]. It is found that the splittings within each of the manifolds are well characterized by the calculation. However, constant energy differences between experiment and calculated groups of resonances were found. Systematic trends in these shifts are then used to evaluate the effect of correlation in these configurations.

There are 14 LS terms of the $3p^4 4s4p$ configuration that originate $J=1$ states [1,2]. Three of these correspond to ^1P terms that are, in principle, the ones that can be excited by a photon starting from the ground state. There are 34 terms in the $3p^4 3d4p$ configuration that originate $J=1$ levels [1]. Six of these correspond to ^1P terms.

The nonrelativistic single-configuration calculation presented here includes the electron-electron Coulomb matrix elements between pairs of terms [4] and the spin-orbit interaction [5]. Numerical values for the Slater integrals and the spin-orbit parameters were obtained directly using the HF single-configuration code [6]. It should be noted that even though some of the parameters in the expressions for both $4s4p$ and $3d4p$ matrix elements are formally the same, their numerical values are different for each configuration. The $3d$ orbital penetrates more than the $4s$ and therefore pushes the $4p$ radial wave function further out. This makes the parameters that do not involve the $4p$ orbital about the same in both configurations, and reduces by as much as 65% the parameters that involve the $4p$ wave function.

The energy levels for the expected dipole-allowed transitions were then calculated by direct addition of the energy eigenvalues to the energy difference between the ground state configuration and the average energy of the corresponding excited configuration. In the discussion that follows the resonances are referred to by number, with number 1 assigned to the lowest energy level of each configuration. These labels are also shown in Figs. 1 and 2.

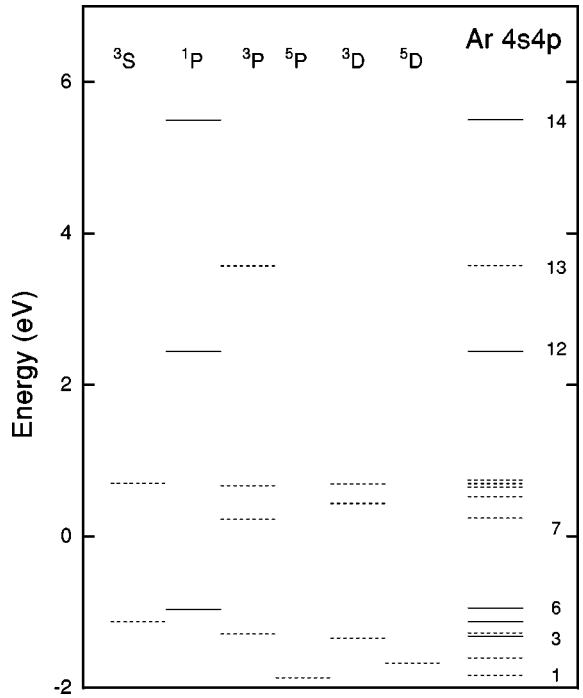

FIG. 1. Energy level diagram of the $J=1$ terms of the $4s4p$ configuration. The first six columns to the left give the position of the terms without spin-orbit interaction. The last column shows the levels found after diagonalization of the Hamiltonian matrix. All levels with more than a 1% component of a ^1P term are indicated by solid lines. All other levels are shown by dashed lines. The numbers to the right are used to identify the resonances in the text.

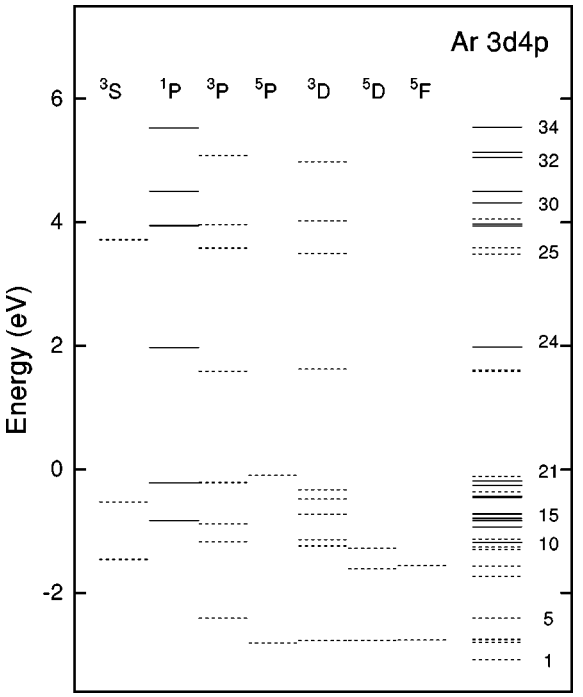

FIG. 2. Energy level diagram of the $J=1$ terms of the $3d4p$ configuration. The first seven columns to the left give the position of the terms without spin-orbit interaction. The last column shows the levels found after diagonalization of the Hamiltonian matrix. All levels with more than a 1% component of a ^1P term are indicated by solid lines. All other levels are shown by dashed lines. The numbers to the right are used to identify the resonances in the text.

Figure 1 shows a comparison between the energy levels for the $4s4p$ configuration obtained without the spin-orbit interaction and with the spin-orbit interaction included. The first six columns to the left of this energy level diagram correspond to pure LS states. The three ^1P terms are the ones in the second column, and are indicated by solid lines. The last column to the right gives the levels obtained by including spin-orbit interaction. The number assigned to each resonance is shown to the right of the plot. The levels with a significant ^1P component are indicated by solid lines also. The only ^1P term that mixes strongly with the other terms, especially with ^3S, ^3P, and ^3D, is the lowest one, and the mixing gives origin to three levels (3, 5, and 6) with more than 1% of ^1P. There is good overall agreement between the results obtained in this work for the $4s4p$ multiplet and those obtained by Baig and Ohno [2] in their relativistic calculation. Closer examination reveals that, except for the lowest level, all the nonrelativistic levels are lower than the relativistic ones, with the largest difference being 0.19 eV for level 12.

Figure 2 shows the corresponding comparison for the $3d4p$ configuration. In this case there are seven different pure LS multiplets which correspond to the seven leftmost columns. Once again, the ^1P terms are indicated by solid lines in the second column. The levels found by taking into account the spin-orbit interaction are shown in the last column to the right. In this case the mixing is stronger, and 17 levels with more than 1% ^1P character were found. They are indicated by solid lines. The numbers assigned to the resonances are shown to the right of the figure.

The comparison between the present calculation and experiment is made in Fig. 3. The theoretical results (dashed lines) are in columns to the left of the experimental values (dotted lines). The experimental results include the new $4s4p$ resonance observed by Caldwell *et al.* [3], and all the $4s4p$ and $3d4p$ resonances reported by Madden, Ederer, and Codling [1]. Arrows indicate the shifts that would match the theoretical with the observed levels. The whole $3s \rightarrow np$ single electron excitations have to be shifted downwards by an almost constant amount (4 eV). The lowest three levels of the $4s4p$ configuration (resonances 3, 5, and 6 in Fig. 1), which in the calculation are much lower than the $3s \rightarrow np$ resonances, are shifted up, maintaining the separation between consecutive lines. These three lines overlap, in terms of their positions, with the $3s \rightarrow np$ series. However, there is no indication of any interaction between these two groups of resonances [3]. The next $4s4p$ level (12 in Fig. 1) is almost pure ^1P and is all alone in the spectrum. Its position is slightly shifted upwards from the calculated value. The last $4s4p$ ^1P level (14 in Fig. 2) is also alone, and is shifted downwards.

The comparison between calculated and observed levels of the $3d4p$ configuration is made in the last two columns to the right of the figure. Levels 10, 12–17, 19, and 20 in Fig. 2 correspond to the lowest observed levels of the configuration [1]. However, the energy difference between experiment and theory does not stay constant for this group of levels. A more detailed discussion of the energy shifts for this group of levels is presented below. Level 24 is almost pure ^1P and is all

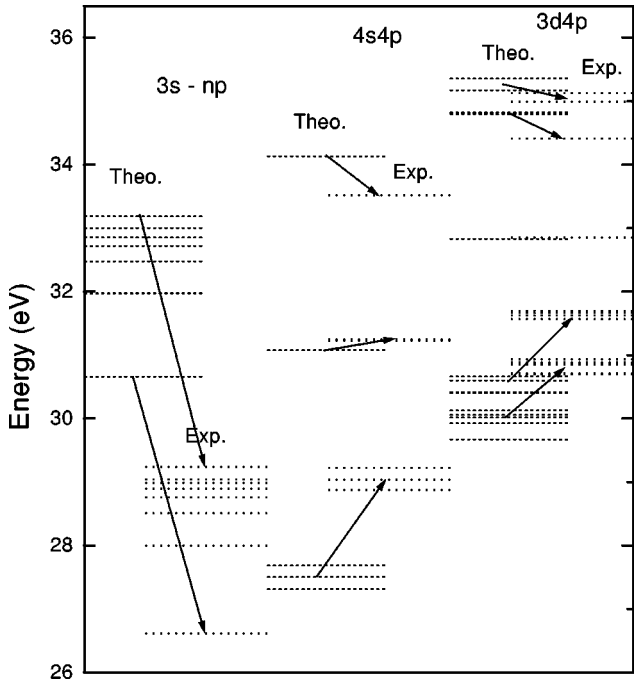

FIG. 3. Comparison between calculated and observed levels. The resonances are grouped in three sets of two columns. The theoretical results are shown in the left column of each group, the position of observed lines is shown in the right column of the group. Group to the left: $3s \rightarrow np$ series. Center group: $4s4p$ configuration. Group to the right: $3d4p$ configuration. The arrows indicate the shift needed in the calculation to match the experiment.

alone both in experiment and in the calculation. The energy difference is the smallest for this level, equal to 0.022 eV. Finally, calculated levels 27, 28, 30, and 31 correspond to the highest observed levels of this configuration. In this case the calculated energies are all above the observed energies.

A one to one correspondence between experiment and theory can be established for most of the lines. There are, however, three exceptions to the one to one correspondence. The first one happens for level 10 of the $3d4p$ configuration calculation, which gives only one line, while the experiment reported a doublet separated by 16 meV [1]. A similar situation is found for level 12 of the $4s4p$ configuration, for which there are two experimental lines separated by 18 meV [1]. Finally, the opposite is found for levels 27 and 28 of the $3d4p$ configuration. The calculation gives two lines with an energy separation of 28 meV, both with significant ^1P contribution, and only one line was found experimentally [1].

This line assignment is confirmed when one considers the difference between the observed and the calculated position of the levels. Levels 3, 5, and 6 of the $4s4p$ configuration make up the first group, with an almost constant energy difference of 1.54 eV. The next group is formed by levels 10–15 of the $3d4p$ configuration. For this group the energy difference between experiment and theory starts at about 1 eV and steadily decreases until it reaches 0.8 eV at level 15. Finally, levels 16–19 form a third group of resonances. In this case the energy difference between experiment and theory starts at about 1.2 eV and also tends to decrease. The behavior of this energy difference for levels 10–20 of the $3d4p$ configuration is shown in Fig. 4. The shift is almost linear for resonances 10–15, with a jump for level 16, and another linear decrease until one reaches level 20.

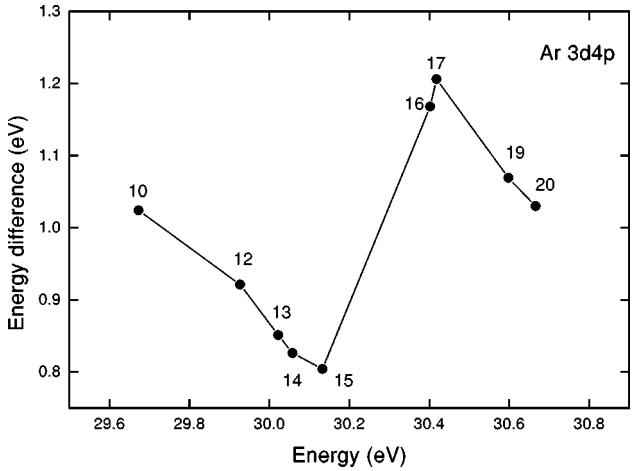

FIG. 4. Energy shift for the lowest two groups of the $3d4p$ configuration (resonances 10, 12–17, 19, and 20 in Fig. 2) as a function of the calculated energy level. See text.

Levels 12 and 14 of the $4s4p$ configuration and all levels above 20 of the $3d4p$ configuration are isolated, thus making it hard to interpret the energy differences. However, a general trend is found, in that the spread in the levels is larger in the calculation than in the experiment, with positive energy separation between experiment and theory for the levels below the average energy of the configuration, and negative differences for the levels above the average energy of the configuration. The effect of the electron-electron correlation is thus a contraction of the spread in the levels belonging to either configuration. One can even calculate the contraction by considering the ratio of the experimental energy spread to the theoretical energy spread. The $4s4p$ configuration spread is reduced to 68% of the theoretical one, and the $3d4p$ configuration is contracted to 78% of the calculation. This contraction is slightly larger than the 80% reduction of the Slater integrals that is commonly employed to take into account the effect of electron-electron correlations in single configuration calculations [7].

Even though the only information about the experimental intensities is found in the densitometer trace (Fig. 4 of Ref. [1]), a few words can be said in terms of the present calculation. Once again, there is good qualitative agreement, in the sense that the resonances with the largest excursions in the experiment correspond to the levels with the largest ^1P contributions. A quantitative discussion of the line shapes and intensities depends, on one hand, on the dipole matrix element between a correlated ground state wave function and the doubly excited state, and on the other on the detailed interaction between the discrete excited levels and several open continua, a calculation that is clearly beyond the scope of this work.

The single-configuration HF calculation performed in this work allowed a direct comparison with the experimental results of Madden, Ederer, and Codling [1], and recent electron spectrometry work [3]. A one to one correspondence between levels was found in most cases. The levels were grouped based on the difference between experiment and theory for the positions of the resonances. Good agreement with experiment was found for the energy splittings within

each group. Finally good overall qualitative agreement was found for the line intensities, with the strongest resonances corresponding with the levels that theory predicts have a larger ^1P component mixed in.

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