Excitation of the metastable states of argon

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Abstract
We have carried out calculations for the excitation from the lowest metastable states of argon (the \( J = 0, 2 \) levels of the \( 3p^54s \) configuration) to the ten higher-lying fine-structure levels of the \( 3p^55p \) configuration, using the relativistic distorted-wave approximation. We report our results for the integrated cross section at energies up to 300 eV.

1. Introduction
Electron impact excitation from the metastable states of the noble gases plays an important role in many practical applications particularly in low temperature plasmas and discharge physics. The accurate knowledge of the cross sections for these transitions is therefore very important. These cross sections are also much larger as compared to excitation from the ground state.

In our previous work we have studied electron impact excitation of the noble gases from their two lowest metastable states (i.e. the \( J = 0, 2 \) states of the \( n^p(n+1)s \) configuration) to the ten higher lying fine structure states of the \( np^5(n+1)p \) configuration with \( J = 0,1,2,3 \) [1]. To study these transitions we used the relativistic distorted-wave approximation (RDW) method which provides a consistent relativistic treatment by solving the Dirac equations for both the bound states of the target electrons and the continuum states of the scattered electron. We reported results for integrated cross sections for electron impact energies up to 400 eV and compared our results with other available theoretical and experimental results.

Recently, there has been progress in the cross section measurements for the electron impact excitation of the metastable states (viz. the \( 3p^34s \) configuration with \( J = 0,2 \)) of argon atoms to the ten fine structure states of \( 3p^55p \) configuration [2]. In the light of this experimental study as well as our continuing application of the RDW method to significant problems in electron excitation of atoms we have extended our work [1] to the calculation of the cross sections for the excitation of these fine-structure transitions.

2. Theory
The distorted-wave T-matrix for the electron impact excitation of an atom having \( N \) electrons and nuclear charge \( Z \) from an initial state \( i \) to final state \( f \) can be written as [1,3] (atomic units are used throughout)

\[
T_{i->f}^{\text{DW}} = \langle \chi_f^- | (1, 2, \ldots, N+1) | V - U_f(N+1) | A\chi_i^+ | (1, 2, \ldots, N+1) \rangle
\]

where \( V \) is the target-projectile interaction given by

\[
V = -\frac{Z}{r_{N+1}} + \sum_{j=1}^{N} \frac{1}{|r_j - r_{N+1}|}
\]

(2)

Here \( r_j \) (\( j = 1, \ldots, N \)) represents the position co-ordinates of the target electrons and \( r_{N+1} \) is the position co-ordinate of the projectile electron with respect to the nucleus of the atom. \( U_f \) is the distortion potential which is taken to be a function of the radial co-ordinates of the projectile electron only, i.e.
Also $U_f$ is chosen to be a spherically averaged static potential of the final state of the atom. This choice of $U_f$ has been shown to yield the most consistent results [4]. The wave functions $\chi_{\alpha}^{(+)}$, where ‘ch’ refers to the two channels, i.e. initial ‘i’ and final ‘f’, are represented as a product of the N-electron target wave functions $\phi_{\alpha}$ and a projectile-electron distorted-wave function $F_{\alpha}^{DW(+)}$, i.e.

$$\chi_{\alpha}^{(+)}(1, 2, \ldots, N+1) = \phi_{\alpha}(1, 2, \ldots, N) F_{\alpha}^{DW(+)}(k_{\alpha}, N+1) \quad (3)$$

Here ‘+’ refers to an outgoing wave while ‘−’ denotes an incoming wave. A is the antisymmetrization operator that takes into account the exchange of the projectile electron with the target electrons and $k_{\alpha}$ are the linear momenta of the projectile electron in the initial and final state. Details of the calculation of the distorted waves are given in [5].

We define the scattering amplitude for the excitation of an argon atom in a metastable $3p^5s$ state with total angular momentum $J_i$ and magnetic quantum number $M_i$ to a final $3p^55p$ state with angular momentum $J_f, M_f$ as

$$f(J_f, M_f, \mu_f; J_i, M_i, \mu_i) = (2\pi)^2 \frac{k_f}{k_i} F_{\alpha}^{DW} (J_f, M_f, \mu_f; J_i, M_i, \mu_i) \quad (4)$$

where $\mu_i$ and $\mu_f$ are the spin projections in the initial and final channels. Then with our normalization of the distorted wave function $F_{\alpha}^{DW(+)}$ the differential cross section (DCS) is given by [5]

$$DCS = \frac{1}{2(2J_i+1)} \sum_{\mu_i, \mu_f, \mu_f, \mu_i} |f(J_f, M_f, \mu_f; J_i, M_i, \mu_i)|^2 \quad (5)$$

and the integrated cross section (ICS) is obtained by integrating the DCS over all scattering angles.

3. Wave Functions

In the nonrelativistic notation the ground state of argon is expressed as $3p^6$ while in the relativistic $j-j$ coupling scheme, this shell is broken into two subshells and represented as $3p^3 3p^3$ where $\bar{p}$ represents a $p$ electron with total angular momentum $j=1/2$, while $p$ has $j=3/2$. In the nonrelativistic representation the lowest lying two metastable states are represented as $3p^34s$ with total angular momentum $J=2$ and $J=0$. These are designated as $1s_1$ and $1s_3$, respectively, in the Paschen notation. Since $s$ electrons have $j=1/2$, the $1s_1$ state with $J=2$ must have the configuration $3p^2 3p^2 4s$ in the $j-j$ coupling scheme while the $1s_3$ state with $J=0$ must have the configuration $3p^2 3p^2 4s$. Thus the hole in the valence shell is different for these two metastable states.

We are considering the electron impact excitation to the ten individual fine-structure levels of the $3p^55p$ manifold. In the $j-j$ scheme these states are linear combinations of the configurations $3p^2 3p^2 5p$ with $J=1, 2; 3p^2 3p^2 5p$ with $J=0, 1, 2, 3; 3p^2 3p^2 5p$ with $J=0, 1$ and $3p^2 3p^2 5p$ with $J=1, 2$. The fine-structure levels are denoted $3p_1$ through $3p_{10}$ in the Paschen notation.
The wave functions for the atomic states were calculated with the GRASP92 program [6]. These wavefunctions for initial and final states are optimized on the basis of the transition energy and oscillator strength. The wave functions for the 3p manifold were calculated within a multiconfiguration Dirac-Fock approximation and included the 4p and 4p orbitals as well as the spectroscopic 5p and 5p orbitals. The wave functions for the final state can be written as the linear combination of the configurations with same J values. The contributions from the various configurations to the fine-structure levels of the final states are given in table 1. This table shows that the J=0 levels of 3p^5 p (i.e. 3p_1 and 3p_3) have significant

| Configurations | 3p^5 3p 4p | 3p^5 3p 4p | 3p^5 3p 5p | 3p^5 3p 4p | 3p^5 3p 5p | 3p^5 3p 5p |
|----------------|-----------|-----------|-----------|-----------|-----------|-----------|
| J = 0 levels   |           |           |           |           |           |           |
| 3p_1           | 0.3048    | -         | 0.5926    | 0.2472    | -         | 0.7034    |
| 3p_3           | 0.1209    |           | 0.7197    | 0.0629    |           | -0.6808   |
| J = 1 levels   |           |           |           |           |           |           |
| 3p_2           | 0.0267    | -0.0288   | 0.1294    | -0.1404   | -0.0006   | -0.0004   |
| 3p_4           | 0.0134    | 0.0139    | 0.0661    | 0.0701    | -0.0139   | -0.0005   |
| 3p_6           | 0.0142    | 0.0116    | 0.7338    | 0.6718    | 0.0239    | 0.0008    |
| 3p_10          | 0.0385    | -0.0435   | -0.6609   | 0.7209    | 0.0223    | -0.0642   |
| J = 2 levels   |           |           |           |           |           |           |
| 3p_3           | -0.0188   | 0.0006    | -0.0831   | 0.0326    | -         | 0.0002    |
| 3p_5           | -0.0004   | 0.0239    | -0.1881   | 0.9806    | -         | 0.0111    |
| 3p_7           | -0.0006   | 4.32e-4   | 0.9783    | 0.1916    | -         | 0.0243    |
| J = 3 level    |           |           |           |           |           |           |
| 3p_9           | -0.0255   |           |           |           |           | 0.9997    |

Table 2. Energy differences (eV) for the transitions considered: NIST - experimental values from the NIST database; GRASP - calculated values using the GRASP92 program.

| Transition | NIST  | GRASP |
|------------|-------|-------|
| 1s_5-3p_10| 2.91564 | 2.84473 |
| 1s_5-3p_5 | 2.95069 | 2.87598 |
| 1s_5-3p_8 | 2.95771 | 2.88965 |
| 1s_5-3p_7 | 2.97656 | 2.91211 |
| 1s_5-3p_6 | 2.98056 | 2.91699 |
| 1s_5-3p_3 | 3.02759 | 3.03809 |
| 1s_5-3p_4 | 3.13229 | 3.08887 |
| 1s_5-3p_3 | 3.13994 | 3.09961 |
| 1s_5-3p_2 | 3.13877 | 3.10156 |
| 1s_5-3p_1 | 3.18976 | 3.42383 |
| 1s_5-1s_3 | 0.17481 | 0.20215 |

| Initial State | NIST | GRASP |
|---------------|------|-------|
| 3p_10         | 1.81e-4 | 2.59e-4 |
| 3p_5          | 3.58e-3 | 3.79e-3 |
| 3p_8          | 7.38e-4 | 1.34e-3 |
| 3p_7          | 4.49e-4 | 7.33e-4 |
| 3p_6          | 3.63e-3 | 5.94e-3 |
| 3p_4          | 3.74e-5 | 4.26e-3 |
| 3p_3          | 1.30e-4 | 4.41e-4 |
| 3p_2          | 6.39e-4 | 1.18e-3 |

Table 3. Dipole oscillator strengths for transitions in Ar: NIST, values from the NIST database; GRASP, present calculations.

The wave functions for the atomic states were calculated with the GRASP92 program [6]. These wavefunctions for initial and final states are optimized on the basis of the transition energy and oscillator strength. The wave functions for the 3p manifolds were calculated within a multiconfiguration Dirac-Fock approximation and included the 4p and 4p orbitals as well as the spectroscopic 5p and 5p orbitals. The wave functions for the final state can be written as the linear combination of the configurations with same J values. The contributions from the various configurations to the fine-structure levels of the final states are given in table 1. This table shows that the J=0 levels of 3p^5 5p (i.e. 3p_1 and 3p_3) have significant
mixing from the $J=0$ levels of 3$p^54p$ configurations whereas all other levels of 3$p^55p$ with $J = 1, 2, 3$ show less mixing with the 3$p^54p$ configurations. The 3$p_1 - 3p_4$ levels come primarily from configurations with a $\bar{p}$ hole in the valence shell and the 3$p_5 - 3p_{10}$ levels from configurations with a $p$ hole in the valence shell.

In table 2 we give the calculated energy differences for the transitions considered here. We also include data from the NIST (http://physics.nist.gov/PhysRefData/ASD/) for the energy differences. From this table we see that as compared to NIST energy levels our 3$p_2$ and 3$p_3$ levels are inverted with a very small energy difference. Table 3 shows results for our calculated dipole oscillator strengths along with values listed in NIST database. Note that there are no allowed dipole transitions to the 3$p$ levels with $J = 0$ and that the only dipole transitions from the 1$s_3$ level are to the 3$p$ levels with $J = 1$.

Our calculated energy differences are accurate to about 3% with the exception of the 1$s_5$-3$p_i$ transition which has the largest energy difference. However, the energy splitting for the 1$s_1$-1$s_5$ is accurate to about 15%. Our values for the oscillator strengths are in reasonable agreement with the NIST values given that the errors in the latter are estimated to be 25%.

4. Results and Discussions

We are considering here the electron impact excitation of argon from its metastable 1$s_3$ and 1$s_5$ states (i.e. the $J = 0, 2$ levels of the 3$p^54s$ configuration) to the ten higher-lying fine-structure states 3$p_i$ (with $i = 1$-10) of the 3$p^55p$ configuration. The integrated cross sections for these transitions have been calculated in the incident energy range from excitation threshold up to 300 eV. In this section we present and discuss these results.

A transition between two fine-structure levels is a dipole allowed transition only if the change in angular momentum between the initial and final states $\Delta J = -1, 0$ or $1$ and the initial and final states do not both have $J = 0$. Thus for excitations from the 1$s_3$ state with $J = 0$, only those transitions to a final state with $J = 1$ are allowed whereas for excitations from the 1$s_5$ state with $J = 2$, all transitions are allowed except those to states with $J = 0$. Integrated cross sections for allowed transitions approach the Bethe-Born form at higher electron impact energies

$$ICS \sim 4\pi a_0^2 \frac{f_{osc}}{E\Delta E} [\ln E + b]$$  \hspace{1cm} (6)

Here $a_0$ is the Bohr radius, $f_{osc}$ is the dipole oscillator strength for the transition, $\Delta E$ is the energy of the transition and $E$ is the energy of the incident electron, and $b$ is a constant. All energies are in atomic units. Also the cross sections for the forbidden transitions behave as

$$ICS = d_0 E^{d_1} a_0^2$$  \hspace{1cm} (7)

at higher energies. We fit equations (6) and (7) to our calculated cross sections and obtain the constants $b$, $d_0$ and $d_1$ which are given in tables 4 and 5. Since the excitation energies for transitions from the metastable states are much smaller than those from the ground state, these fittings are valid at energies as low as 30 eV and the maximum error in the fittings is always less than 5% over the range from 30 to 300 eV. The advantage of the expressions (6) and (7) is that one can obtain the cross sections at any desired higher energies. From table 4 we can see that the cross sections for the forbidden transitions considered here behave as $E^3$ as $E$ increases. We note that the cross sections for excitation to the final state with $J = 3$ from 1$s_3$ state with $J=0$ are identically zero in our approximation from angular momentum coupling considerations and therefore this transition does not appear in table 5.
In order to further discuss the nature of the cross sections in the entire energy range, we present our results in figure 1 for all the transitions from the 1\textit{s}\textsubscript{3} and 1\textit{s}\textsubscript{5} metastable states. The dipole allowed and forbidden transitions are of two types on the basis of core changing nature of the transition. Figure 1(a) and 1 (c) display the results for the transitions where the final states have \textit{p} as hole. Here excitations from the 1\textit{s}\textsubscript{5} level are core changing but not from the 1\textit{s}\textsubscript{3} level while figure 1 (b) and 1 (d) show the results for the transitions where the final states have \textit{p} as hole and the excitations from 1\textit{s}\textsubscript{3} level are core changing but not from the 1\textit{s}\textsubscript{5} level.

In figure 1 (a) and 1 (b), we show the behavior of the cross sections for the dipole allowed transitions. We expect these transitions to have a large cross section but some of these, e.g. 1\textit{s}\textsubscript{3} - 3\textit{p}\textsubscript{7}, are quite small. The reason for this is that this is two electron transition. The valence electron changes from 4\textit{s} to 5\textit{p} while the core changes from having a 3\textit{p} hole in the 1\textit{s}\textsubscript{3} level to a 3\textit{p} hole in the dominant configurations of the 3\textit{p}\textsubscript{7} level. Thus in a first-order theory such as RDW the contribution of this excitation process to the direct term of the T-matrix is zero and hence the only contribution to the T-matrix will be from the exchange terms and also from other configurations mixed with the one indicated. Therefore, as shown in figure 1 (a) the allowed cross sections for excitation from the 1\textit{s}\textsubscript{5} state to different 3\textit{p} levels with \textit{p} as hole will be small as compared to the cross sections for the excitation from 1\textit{s}\textsubscript{3} state to these levels.

Similarly, figure 1 (b) clearly shows that in case of the excitations to the states with \textit{p} as hole, larger cross sections are obtained when excitation occurs from 1\textit{s}\textsubscript{5} state. We also note that the ICS should be proportional to the optical oscillator strength divided by the transition energy at higher energies for allowed transitions. Since the transition energies are nearly the same for all transitions the magnitude of the fine-structure cross sections are determined primarily by the optical oscillator strength for allowed transitions. A notable exception to this occurs in the excitation of the 3\textit{p}\textsubscript{10} level where the oscillator strength of the transition from the 1\textit{s}\textsubscript{5} state is more than six times larger than that from the 1\textit{s}\textsubscript{3} state in spite of the fact that it is a core-changing transition. Nevertheless, the cross section for excitation from the 1\textit{s}\textsubscript{5} level shown in figure 1 (b) is larger than that from the 1\textit{s}\textsubscript{3} level because of the large value of the parameter \textit{b} given in table 4. However, at very large energies the 1\textit{s}\textsubscript{5} cross section would dominate. Our calculations show that contributions from the 4\textit{p} configurations in the 3\textit{p}\textsubscript{10} wave function are primarily responsible for this large value of the oscillator strength.

Figure 1 (c) and 1 (d) contain the results for the forbidden transitions. These cross sections are much smaller than those for allowed transitions at larger energies, but at energies near threshold they have comparable magnitude. Again, as described earlier, the cross sections for core changing transitions will

| Initial State | 1s\textsubscript{5} | 1s\textsubscript{3} |
|---------------|----------------|----------------|
| Final State   | \textit{b}   | \textit{b}   |
| 3p\textsubscript{10} | 64.58906 | 0.54482 |
| 3p\textsubscript{9}  | 17.93634 | - |
| 3p\textsubscript{8}  | 12.93348 | - |
| 3p\textsubscript{7}  | 9.04251 | 0.31103 |
| 3p\textsubscript{6}  | 8.31014 | - |
| 3p\textsubscript{4}  | 3.03180 | 14.74327 |
| 3p\textsubscript{3}  | 3.29046 | - |
| 3p\textsubscript{2}  | 3.30142 | 11.18358 |

| Initial State | 1s\textsubscript{5} | 1s\textsubscript{3} |
|---------------|----------------|----------------|
| Final State   | \textit{d}\textsubscript{0} | \textit{d}\textsubscript{1} |
| 3p\textsubscript{8} | - | - |
| 3p\textsubscript{6} | - | - |
| 3p\textsubscript{3} | 1.27e-3 | -3.07484 |
| 3p\textsubscript{1} | 2.17e-3 | -3.07484 |

In order to further discuss the nature of the cross sections in the entire energy range, we present our results in figure 1 for all the transitions from the 1\textit{s}\textsubscript{3} and 1\textit{s}\textsubscript{5} metastable states. The dipole allowed and forbidden transitions are of two types on the basis of core changing nature of the transition. Figure 1(a) and 1 (c) display the results for the transitions where the final states have \textit{p} as hole. Here excitations from the 1\textit{s}\textsubscript{5} level are core changing but not from the 1\textit{s}\textsubscript{3} level while figure 1 (b) and 1 (d) show the results for the transitions where the final states have \textit{p} as hole and the excitations from 1\textit{s}\textsubscript{3} level are core changing but not from the 1\textit{s}\textsubscript{5} level.
have smaller magnitude than those where core does not change and also the cross sections for all the forbidden transitions fall off like $1/E^3$ at higher energies.

**Figure 1.** Integrated cross sections for electron excitation of argon: (a) the solid curve $1s_3 - 3p_2$, the dashed curve $1s_5 - 3p_4$, the dotted curve $1s_5 - 3p_6$, the dashed-dot curve $1s_5 - 3p_2$, and the dashed-double-dot curve $1s_5 - 3p_4$ transitions; (b) the solid curve $1s_3 - 3p_7$, the dashed curve $1s_3 - 3p_9$, the dotted curve $1s_5 - 3p_10$, the dotted double-dot curve $1s_5 - 3p_8$, the short-dot curve $1s_5 - 3p_9$, the short-dashed curve $1s_5 - 3p_10$ transitions; (c) the solid curve $1s_3 - 3p_5$, the dashed curve $1s_3 - 3p_7$, the dotted curve $1s_5 - 3p_8$, the dashed-dot curve $1s_5 - 3p_9$, the dashed double-dot curve $1s_5 - 3p_10$ transitions; (d) the solid curve $1s_3 - 3p_5$, the dotted curve $1s_3 - 3p_7$, the dashed curve $1s_5 - 3p_8$ transitions.

**5. Conclusions**

We have used our RDW approximation along with Dirac-Fock wave functions from the GRASP92 program to study electron excitation of the lowest lying metastable states of argon to the ten higher lying fine structure states of the $3p^5 5p$ manifold. We have shown that the Dirac-Fock approximation yields reliable results for energies and oscillator strengths for most of the transitions studied. We have given a detailed analysis of the individual fine-structure transitions which are reflected in our results. We hope that our present theoretical study will be able to supplement experimental work in this direction.
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