EXCITATION CROSS SECTION FOR SOME OF THE DOUBLY IONIZED STATES OF ARGON, NEON AND KRYPTON BY FAST ELECTRONS

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ABSTRACT

Excitation cross section for the doubly ionized states of argon, neon and krypton has been found for the process where a fast moving free electron impinges upon a neutral atom causing the neutral atom to go from ℓ^N to $(\ell^{N-3} - n\ell'')$ in a very short time compared to the relaxation time of the ion.

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I.   INTRODUCTION

It has been shown[1,2,3] that the method of sudden perturbation can account for the excitation of some of the excited states of argon II in the pulsed argon laser. This method of calculation yields correct results only when the Hamiltonian changes from an initial state to a final state in a very short time compared to the relaxation time of the system.[5] In this method, the eigenfunctions of the unperturbed Hamiltonian are expanded in terms of the eigenfunctions of the perturbed system. In the problem that we are considering, we assume that a neutral atom with an ℓ^N outer shell configuration loses m(m=2) of its ℓ^N electrons, in a very short time compared to the relaxation time of the atom, after making a collision with a fast impinging electron. Before collision, the eigenfunction of the system consists of the product of a free electron wave function with that of the product of a free electron wave function with that of the bound atomic electrons. After collision, the new eigenfunctions are the product of the wave function of (m+1) free electron, with those of ℓ^{N-m} bound atomic electrons. Two cases are considered. For the first case, it is assumed that the atom makes a collision with a fast-moving electron, loses two of its N outer shell electrons, and is simultaneously excited, i.e., $\ell^N \rightarrow (\ell_n^{N-3}-n\ell)$. There the atom is doubly ionized and excited at the same time. For the second case, it is assumed that two collisions are involved, i.e., the atom makes a collision and goes to an excited single ionized configuration $(\ell_{1n}^{N-2}-n\ell')$; then, though another collision, it may lose its excited $n\ell'$ electron or one of the ℓ_n^{N-2} core electrons. This process is important when $(\ell_{1n}^{N-2}-n\ell')$ is a metzstable state or a state with relatively long life time. The states for which excitation cross sections will be found are $|\ell^3, \phi_2, n\ell_s''; {}^3P_J\rangle$, $|\ell^3, \phi_2, n\ell_s''; {}^1D_2\rangle$ and $|\ell^3, \phi_2, n\ell_s ; {}^1S_O\rangle$ with $\phi_2 = {}^4S, {}^2D$ or ${}^2P$.

To obtain the probability of production of any one of the new states, we have to expend the unperturbed Hamiltonian eigenfunctions in terms of the complete set of eigenfunctions of the new Hamiltonian. The overlap integrals in these calculations involve those between electronic bound states before and after collision and between bound and resulting free electronic states. The absolute-square values of the former set of integrals are proportional to the excitation cross section, whereas the corresponding values for the latter set are proportional to the ionization cross section. Since experimental double ionization cross sections for

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most of the atoms are known, the excitation cross section for case one can be calculated exactly.

For example, for the $3p^6$ outershell configuration of neutral argon to go to the $3p^3$ - $4p$ state after collision with a 100 ev electron, we find a cross section of 8.9×10^{-19} cm^2. In what follows we shall attempt to find expressions for the cross sections of the various excited states. These states are represented by their angular momentum quantum numbers, i.e., states of the form $|\ell^{N-3}\phi_2, n\ell''s; \phi_1\rangle$. For noble gas atoms where N=6, $\ell = \ell'' = 1$ we have $\phi_2 \equiv {}^4S$, ${}^2P$ or ${}^2D$ and ϕ_1 can be ${}^1S_1$, ${}^3P_{0,1,2}$ or ${}^1D_2$. We shall calculate cross sections for all the 12 possible combinations of ϕ_2 and ϕ_1. Figure 1.

II.   CALCULATION

Case One

We now assume that the atom makes a collision with an electron and loses two of its electrons, simultaneously. In order to know the possible excited states, we have to expand the unperturbed eigenfunctions $1\ell^N\phi_0; F_{1i}\rangle$ in terms of the eigenfunctions of the perturbed Hamiltonian. This eigenfunction consists of the product of $|\ell^N\phi_0\rangle$ bound wave function and the F_{1i} free electron wave function. We have, after expansion

(1a) $$|\ell^N\phi_0; F_{1i}\rangle = \sum_{n,f} a_{nf} |\ell_n^{N-3}\phi_2; n\ell''s, \phi_1': F_{1f}, F_{2f}, F_{3f}\rangle ,$$

where $|\ell_n^{N-3}\phi_2; n\ell''s, \phi_1'\rangle$ is an excited doubly ionized state of the atom, $n\ell''$ is the excited electron, and ℓ_n are the core electrons. The subscript n indicates that the radial wave function of ℓ_n^{N-3} core electrons changes as the principal quantum number n of the excited electron assumes different values. In Eq. (1a), s stands for the spin $1/2$ of the electron, and ϕ with or without super- or subscript stands for the corresponding angular wave functions. For example, in $\ell^{N-3}\phi_2$, ϕ_2 replaces L_2, S_2, M_{L_2} and N_{S_2}, where L_2 is the total orbital angular momentum, S_2 is the total spin-angular momentum, and M_{L_2} and N_{S_2} are the projections of L and S on the magnetic z-axis. F_{1f}, F_{2f} and F_{3f} represent the wave functions for the three free electrons after the impact. The summation in Eq. (1a) is over all the possible final states, F. For Eq. (1) we have

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(1b) $$\sum_f a_{nf} = \sum_f < \ell_n^{N-3} \phi_2, n\ell''s, \phi_1' : F_{1f}, F_{2f}, F_{3f} | \ell^N \phi_0 : F_{1i} > \ .$$

To calculate these inetrix elements, we first expand the bound atomic wave function $| \ell^N \phi_0 >$ in terms of its parents and grandparents and then decouple two electrons, in other words we have

(2a) $$| \ell^N \phi_0 > = \sum_{\phi, \phi_1} (\ell^{N-1} \phi \ \{| \ell^N \phi_0)(\ell^{N-2} \phi_1 \ \{| \ell^{N-1} \phi)$$

$$| \ell^{N-2} \phi; \ell s; \ell s, \phi_0 >$$

where two electrons have been separated from the core. The eigen-functions in Eq. (2a) can be decoupled to give us,

(2b) $$| \ell^N \phi_0 > = \sum_{\substack{\phi, \phi_1, ML, M\ell, ML_1, \\ NS, Ns, NS_1, M\ell_2, Ns_2}} (-)^{L+L_1 - 2\ell + ML_0 + ML + S + S_1 - 2S + NS_0 + NS}$$

$$\{[L_0] \ [L] \ [S_0] \ [S]\}^{\frac{1}{2}} (\ell^{N-1} \phi \ \{| \ell^N \phi_0) \ (\ell^{N-2} \phi_1 \{| \ell^{N-1} \phi)$$

$$\begin{pmatrix} L & \ell & L_0 \\ ML & M\ell_1 & ML_0 \end{pmatrix} \begin{pmatrix} L_1 & \ell & L \\ ML_1 & M\ell_2 & ML \end{pmatrix} \begin{pmatrix} S & s & S_0 \\ NS & Ns_1 & NS_0 \end{pmatrix} \begin{pmatrix} S_1 & s & S \\ NS_1 & Ns_2 & NS \end{pmatrix}$$

$$| \ell^{N-2} \phi_1 > \ | \ell s, M\ell_1 Ns_1 > \ | \ell s, M\ell_2 Ns_2 > \ ,$$

where the symbol $[x] = 2x+1$, ϕ_n stands for L_n, S_n, ML_n and Ns_n. Replacing Eq. (2a) back in Eq. (1) we obtain

(2c) $\quad \sum_f a_{nf} = \sum_{\phi, \phi_1} (\ell^{N-2}\phi_1 \{ | \ell^{N-1}\phi)(\ell^{N-1}\phi \{ | \ell^N\phi_0)$

$$\langle \ell_n^{N-3}\phi_2, n\ell''s, \phi_1' | \ell^{N-2}\phi_1 \rangle$$

$$\times \left\{ \sum_{\substack{M_L, M_{\ell_1}, M_{L_1}, M_{\ell_2} \\ N_S, N_s, N_{S_1}, N_{S_1}, f}} (-1)^{L+L_1 - 2\ell + M_{L_O} + M_L + S + S_1 - 2s + N_{S_O} + N_S} \right.$$

$$\{[L_O][L][S_O][S]\}^{\frac{1}{2}}$$

$$\begin{pmatrix} L & \ell & L_O \\ M_L & M_{\ell_1} & M_O \end{pmatrix} \begin{pmatrix} L_1 & \ell & L \\ M_{L_1} & M_{\ell_2} & M_L \end{pmatrix} \begin{pmatrix} S & s & S_O \\ M_S & M_{s_1} & M_{S_O} \end{pmatrix} \begin{pmatrix} S_1 & s & S \\ M_{S_1} & M_{s_2} & M_S \end{pmatrix}$$

$$\left. \times \langle f_{1i} | f_{1f} \rangle \langle \ell_s, M_{\ell_1}, N_{s_1} | f_{2f} \rangle \langle \ell_s, M_{L_2} N_{s_2} | F_{3f} \rangle \right\} \quad .$$

In the above equation the absolute square value of the quantity in braces
({}) is proportional to the double ionization probability of the atom. It
consists of the product of an initially free electron and two bound
electrons with the wave functions of three free electrons. In Eq. (2c),
one more matrix element remains to be calculated, and that is the
quantity

(2d) $\quad \langle \ell_n^{N-3}\phi_2; n\ell'', \phi_1' | \ell^{N-2}\phi_1 \rangle$

$$= \sum_{\substack{\phi_2', M_{L_2}, M_{\ell''}, M_{L_2}' \\ M_\ell N_{S_2}, N_{S_2}', N_s}} (-1)^{L_2 + L_2' - \ell'' - \ell + M_{L_1}' + M_{L_1} + S_{2_1} + S_2' - 2s + M_{S_1}' + M_{S_1}}$$

$$\{[L_1'][L_1][S_1'][S_1]\}^{\frac{1}{2}} \quad \times$$

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$$\times \begin{pmatrix} L_2 & \ell'' & L_1' \\ M_{L_2} & M_{\ell''} & M_{L_1'} \end{pmatrix} \begin{pmatrix} S_2' & s & S_1' \\ N_{S_2} & N_S & N_{S_1'} \end{pmatrix} \begin{pmatrix} L_2' & \ell & L_1 \\ M_{L_2'} & M_\ell & M_{L_1} \end{pmatrix} \begin{pmatrix} S_2' & s & S_1 \\ N_{S_2'} & N_S & N_{S_1} \end{pmatrix}$$

$$\times (\ell^{N-3}\phi_2 \{ | \ell''^{N-2}\phi_1) < n\,\ell''s, M_{\ell''} N_S | \ell s, M_\ell N_S >$$

$$< \ell_n^{N-3}\phi_2 | \ell^{N-3}\phi_2 >$$

or

(2e) $\quad < \ell_n^{N-3}\phi_2, n\ell''s, \phi_1' | \ell^{N-3}\phi_1 > = (\ell^{N-3}\phi_2 \{ | \ell^{N-2}\phi_1) \int_0^\infty f_\ell(r) F_{n\ell''}(r)\, dr$

$$\times \left[\int_0^\infty f_\ell(r) F_{\ell n}(r)\, dr \right]^{N-3} \delta(\phi_1, \phi_1')\ \delta(\phi_2, \phi_2')\ \delta(\ell, \ell'')\ \delta(\ell_n, \ell) .$$

Of course, the results of Eq. (2d) could have been intuitively clear except for the coefficient in front of the integrals. In Eq. (2e) $f_\ell(r)$ is the radial wave function of one of the $|\ell^N\phi_0>$ neutral ground state atoms; $f_{n\ell}(r)$ and $f_{\ell n}$ are the wave functions of the excited runing electron and the corresponding core electrons of the $|\ell_n^{N-3}\phi_2, n\ell''s\ \phi_1'>$ doubly ionized configuration. In Eqs. (2a) through (2c) the quantities $(\ell^{N'}\psi\{|\ell^{N'-1}\phi)$ are the coefficients of fractional parentage (6) and the symbols in large parentheses are the usual 3 - j symbols.[7]

The probability that the doubly ionized atom will be in an excited state of the form $|\ell_n^{N-3}\phi_2, n\ell''s, \phi_1>$ would be proportional to $|a_n|^2$, where

(3a) $\quad a_n = \sum_f a_{nf}$.

This means we have to calculate the quantities in braces of Eq. (2c) or, in other words, sum over expressions of the form $<f_2 | \ell s\ M_\ell\ M_S>$, which are the overlap integrals between the bound electronic states and all the possible final states of the free electron. We can, however, avoid these calculations by using the experimentally available total cross section data for removing two electrons from the atom. If we represent the double ionization cross section by $Q^{++}(E)$, where E represents the energy of the intial free electron state $|f_i i>$, then from Eqs. (2c), (2e), and (3a)

we have for the excitation cross section of the state $\left| \ell^{N-3}\phi_2, n\ell''s, \phi_1 \right>$ from the ground state $\left| \ell^N \phi_0 \right>$, after impinging with an electron having a kinetic energy E,

$$(3b) \qquad Q_n(E) = \left\{ \sum_\phi (\ell^{N-3}\phi_2 \{| \ell^{N-2}\phi_1)(\ell^{N-2}\phi_1 \{| \ell^{N-1}\phi)(\ell^{N-1}\phi \{| ^N\phi_0) \right.$$

$$\times \int_0^\infty f_\ell(r)\, f_{n\ell''}(r)\, dr \times \left[\int_0^\infty f_\ell(r)\, f_{\ell n}(r)\, dr \right]^{N-3} \Bigg\}^2$$

$$Q^{++}(E)\, \delta(\ell,\, n\ell'')\, \delta(\ell,\, \ell n),$$

where $Q_n(E)$ gives the excitation cross section for the $\left| \ell_n^{N-3}\phi_2, n\ell''s\ \phi_1 \right>$ configuration, the $N-3\ \ell_n$ electrons couple to give ϕ_2 i.e., L_2, S_2; then these angular momenta couple with ℓ'' to give L_1, S_1, M_1, N_1 or ϕ_1. For the case of Noble gas atoms, which are of interest to this paper, $\ell = \ell_n = n\ell'' = 1$, $N = 6$ and the only possible $L_2 S_2$ states are $^2D, ^2P$ or ^4S.[8] The possible final $L_1 S_1$ states would be $^1D, ^3P$ or ^1S. This is seen from Eq. (2e). Moreover, the summation over ϕ in Eq. (3b) breaks down since in the case of ℓ^5 only one possible ϕ state can exist, namely $^2\underline{P}$.

So far neither the coefficients of fractional parentage nor anything in Eqs. (3b) or (3c) gives us any information about the total angular momentum $J = L + S$ of the excited state or its excitation cross section. In the above example, for the noble gas atoms we find that the only possible excited states, when two electrons are removed from an outer p^6 shell, are $\left| \ell'^3\phi_2, n\ell''s, {}^1D \right>$, $\left| \ell^3\phi_2, n\ell''s, {}^3\underline{P} \right>$, or $\left| \ell'^3\phi_2, n\ell''s, {}^1S \right>$, with ϕ_2 assuming any of the three possible states of ℓ'^3. In this example, ^1D_J has a $J = 2$ and ^1S_J has a $J = 0$, but in ^3P_J, J can assume the value of 1, 2 or 0. In general, to find the probability of excitation for any J we have to change the order of coupling of the angular momenta of the expression in Eq. (2a) from LS to jj coupling, i.e.,

$$(4a) \qquad \left| \ell^N \phi_0 \right> = \sum_{\phi_1, \phi} (\ell^{N-1}\phi \{| \ell^N\phi_0)\, (\ell^{N-2}\phi_1 \{| \ell^{N-1}\phi)$$

$$\times \left| \ell^{N-2}L_1 S_1; \ell_1 s_1, LS; \ell_2 s_2\, L_0 S_0 J_0 \right>,$$

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(4b)
$$|\ell^N \phi_o\rangle = \sum_{\phi,\ \phi_1} (\ell^{N-1}\phi\ \{|\ell^N\ \phi_o) (\ell^{N-2}\phi_1\ \{|\ell^N\phi) \sum_{J,J_1 j_1 j_2}$$

$$\{[L_o]\ [S_o]\ [L]\ [S]\ [J]\ [J_1]\ [j_1]\ [j_2]\}^{\frac{1}{2}} \begin{Bmatrix} L & \ell_2 & L_o \\ S & s_2 & S_o \\ J & j_2 & J_o \end{Bmatrix}$$

$$\begin{Bmatrix} L_1 & \ell_1 & L \\ S_1 & s_1 & S \\ J_1 & j_1 & J \end{Bmatrix} \times |\ell^{N-2}L_1 S_1 J_1;\ \ell_1 s_1 j_1, LSJ\ ;\ \ell_2 s_2 j_2,\ J_o M_o\rangle\ .$$

In the above equations $j_n = \ell_n + s_n$, the quantities in curly brackets are the 9-j symbol, and to distinguish the two separated electrons, for the purpose of summation, a subscript is added. As in Eq. (2b) we can uncouple the eigenfunction $|\ell^{N-2}L_1 S_1 J_1;\ \ell_1 s_1 j,\ LSJ\ ;\ \ell_2 s_2 j_2,\ J_o M_o\rangle$ in terms of 3-j symbols and a product of the three wave functions, namely, $|\ell^{N-2}L_1 S_1 J_1 M_1\rangle\ |\ell_1 s_1 j_1 M_{j_1}\rangle\ |\ell_2\ s_2\ j_2\ M_{j_2}\rangle$. Using instead the jj coupled eigenfunctions, Eq. (2c) becomes

(4c)
$$\sum_f a_{nfJ_1} = \sum_{\phi,\phi_1,J,j_1,j_2} (\ell^{N-2}\phi_1\ \{|\ell^{N-1}\phi) (\ell^{N-1}\phi\ \{|\ell^N\phi_2)$$

$$\{[L_o]\ [S_o]\ [L]\ [S]\ [J]\ [J_1]\ [j_1]\ [j_2]\}^{\frac{1}{2}}$$

$$\begin{Bmatrix} L & \ell_2 & L_o \\ S & s_2 & S_o \\ J & j_2 & J_o \end{Bmatrix} \begin{Bmatrix} L_1 & \ell_1 & L \\ S_1 & s_1 & S \\ J_1 & j_1 & J \end{Bmatrix}$$

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$$\times \; <\ell_n'^{N-3} \; L_2 \, S_2 \, j_2 \; ; \; n\ell''s, \; L_1' S_1' J_1' M_1' \, | \, \ell^{N-2} L_1 S_1 J_1 M_1> \quad \times$$

[summation over all final states of the overlap integrals and some 3-j symbols] .

In Eq. (4c) we have added an extra index J_1 to the coefficients a_{nf} to designate the total angular momentum of the excited state. As before, the last term in brackets is simply the overlap integrals and is proportional to the double ionization cross section, and the first portion gives the excitation probability. The excitation cross section to any state of the form $|\ell_n^{N-3} \; L_2 \, S_2 \, J_2 \; ; \; n\ell''sj, \; J_1 M_1>$ from the ground state $|\ell^N \phi_o>$ is,

$$(5) \qquad Q_{nJ_1} = \left\{ \sum_{\phi} \sum_{J, j_1, j_2} (\ell^{N-2}\phi_2 \{ | \ell^{N-2}\phi_1) (\ell^{N-2}\phi_1 \{ | \ell^{N-1}\phi) \right.$$

$$(\ell^{N-1}\phi \{ | \ell^N \phi_o)$$

$$\times \; \{ [L_o] \, [S_o] \, [L] \, [S] \, [J] \, [J_1] \, [j_1] \, [j_2] \}^{\frac{1}{2}}$$

$$\begin{Bmatrix} L & \ell_2 & L_o \\ S & s_2 & S_o \\ J & j_2 & J_o \end{Bmatrix} \begin{Bmatrix} L_1 & \ell_1 & L \\ S_1 & s_1 & S \\ J_1 & j_1 & J \end{Bmatrix} \quad \int_0^\infty f_\ell(1) \, f_{n\ell''}(r) \, dr$$

$$\times \left[\int_0^\infty f_\ell(r) \, f_{\ell n}(r) \, dr \right]^{N-3} \Bigg\}^2 \; Q^{++}(E) \; \mathcal{E}(\ell, \ell n) \; \mathcal{E}(\ell, n\ell'') \; .$$

For the calculations of the radial integrals, a self-consistant Hartree-Fock computer program in the Slater approximation was used, [10] and the results for neon, argon, and krypton are given in Table I. As an illustration, we have calculated the excitation cross section for all the $3p^3$-4p configuration of argon III, and this is presented in Table II. The total cross section for having a $3p^3$-4p configuration after collision with a 100 ev electron is about 0.88×10^{-18}, and this is divided among all the possible angular momentum states permissible from the $3p^3$-4p configuration.

Case Two

Here we assume that the atom loses one electron through collision, and assumes an excited configuration of the form $(\ell_{1n}^{N-2}, n\ell_1)$. Then, through another collision, loses the excited $n\ell_1$ electron or one of the ℓ^{N-2} core electrons to assume a final $(\ell^{N-3}, n\ell'')$ configuration, where N is the total number of electrons in the valence shell. Having seen the principle of the calculations for case one, we can now write the cross section without going through the detailed mathematics, the only difference being that one has to go twice through equations of the form Eq. (2c). Figure 2 shows schematically what happens.

In the second collision where the excited running electron is lost, we have for the excitation cross section of the state $|\ell_{2m}^{N-3}\phi_2, \phi_1\rangle$

$$(6) \qquad Q_1(E,E') = \left\{ \sum_{\phi,\phi_1} (\ell^{N-3}{}_{12} \{| \ell^{N-2}\phi_1)(\ell^{N-2}\phi_1 \{| \ell^{N-1}\phi) \right.$$

$$(\ell^{N-1}\phi\{ \ \ell^{N}\phi_0) \int_0^\infty f_\ell(r) \ f_{n\ell_1}(r) \ dr$$

$$\times \left[\int f_\ell(r') \ f_{\ell_{1n}}(r') \ dr' \right]^{N-2}$$

$$\times \int_0^\infty f_{\ell_{1n}}(r'') \ f_{m\ell_2}(r'') \ dr \times \left[\int_0^\infty f_{\ell_{1n}}(r) \ f_{\ell_{2m}}(r) dr \right]^{N-3} \left. \right\}^2$$

$$Q^+(E) \ Q^+_{n\ell_1}(E') \ \delta(\ell, \ell_{1n}) \ \delta(\ell, n\ell) \ \delta(\ell, m\ell_2) \ \delta(\ell, \ell_{2m}) \quad,$$

where $Q^+(E)$ is the usual single ionization cross section and $Q^+_{N\ell_1}(E')$ is the ionization cross section for removing the $n\ell_1$ excited electron from the $(\ell_{1n}^{N-2}, n\ell_1)$ configuration. $Q_{n\ell_1}$ could be very large as the excited $n\ell_1$ electron assumes higher orbits. The first set of the two integrals in Eq. (6) gives the overlap integrals for the bound states when after a collision $\ell^N \rightarrow (\ell_{1n}^{N-2}, n\ell_1)$, while the second set of the integrals give the overlap integrals for the $(\ell_{1n}^{N-2}, n\ell_1) \rightarrow (\ell_{1n}^{N-2}) \rightarrow (\ell_{2m}^{N-3}, m\ell_2)$ situation. The possible final states are exactly the same as those given in case one, namely, $|\ell^3\phi_2; m\ell_2 s, \phi_1\rangle$, where ϕ_1 is a $^3P, ^1D$, or a ^1S state. Tables III and IV give the radial integrals for the above two processes.

Now, if in the second collision, instead of the excited electron a core electron is removed, i.e., if $(\ell_{1n}^{N-2}, n\ell_1)$ goes into the intermediate state $(\ell_{1n}^{N-3}, n\ell)$, the total orbital and spin angular momenta of the final states will not be evident as in the previous cases. We have to change the order of coupling of the electrons of the excited singly ionized atom. After having separated the electron which has to be lost from the core i.e., by expressing the state in terms of coefficients of fractional parentage,

$$(7a) \qquad |\ell_{1n}^{N-2}\, L_1 S_1; \, n\ell_1\, s, \, LSJ\rangle = \sum_{\phi_2} (P^{N-3}\phi_2 \{|P^{N-2}\phi_1)$$

$$\times \quad |\ell_{1n}^{N-3}\, L_2 S_2; \, \ell_{1n}s, \, L_1 S_1; \, n\ell_1\, s, \, LSJ\rangle ,$$

we then change the order by first coupling the excited $n\ell_1 s$ electron to the $L_2 S_2$ core states and then couple the separated $\ell_{1n}s$ core electron to the resultant states to obtain the final LSJ states, i.e.,

$$(7b) \qquad |\ell_{1n}^{N-2}\, L_1 S_1; \, n\ell_1\, s, \, LSJ\rangle = \sum_{\phi_2} (P^{N-3}\phi_2 \{|P^{N-2}\phi_1) \sum_{\overline{L}\,\overline{S}} \{[\overline{L}]\,[\overline{S}]\}^{\frac{1}{2}}$$

$$\begin{Bmatrix} L_2 & L & \overline{L} \\ n\ell_1 & \ell_{1n} & L_1 \end{Bmatrix} \begin{Bmatrix} S_2 & S & \overline{S} \\ s & s & S_1 \end{Bmatrix} |\ell_{1n}^{N-3}\, L_2 S_2; \, n\ell_1 s, \, \overline{L}\,\overline{S}; \, \ell_{1n}s, \, LSJ\rangle$$

where the quantities in large curly brackets are the 6-j symbols.[8] Now we use Eq. (7b) to calculate the overlap integrals between this singly ionized state and the doubly ionized states. The matrix element involved is,

$$(7c) \qquad \langle\ell_{1n}^{N-2}\phi_1; n\ell_1 s, \phi: F_{1i} |\ell_{2m}^{N-3}\phi_2; m\ell_2\, \phi_1'; \, F_{1f}, \, F_{2f}\rangle$$

$$= \left\{ \alpha \sum_f \langle\ell_{1n}s | F_{2f}\rangle \langle F_{1i}|F_{1f}\rangle \right\}$$

$$\times \int_0^\infty f_{n\ell_1}(r)\, f_{m\ell_3}(r)\, dr \times \left[\int_0^\infty f_{\ell_{1n}}(r)\, f_{\ell_{2m}}(r)\right]^{N-3}$$

$$\delta(\phi_1, \overline{\phi})\, \delta(n\ell_1, m\ell_2)\, \delta(\ell_{1n}, \ell_{2m})$$

where α replaces all the 3-j symbols and summartions over them. It is seen that the only possible excited states are the $\overline{\phi}$ states, namely $\overline{LS}$. From Eqs. (7b) and (7c) we can now write the excitation cross section for all the states $|\ell_{3m}^{N-3}\phi_2, m\ell_3 s \overline{\phi}>$, where $\overline{\phi}$ stands for $\overline{LS}$,

$$(8) \quad Q_2(E, E) = \left\{ \sum_\phi (\ell^{N-3}\phi_2 \{|\ell^{N-2}\phi_1) (\ell^{N-2}\phi_1 \{|\ell^{N-1}\phi) (\ell^{N-1}\phi\{|\ell^N\phi_o) \right.$$

$$[\overline{L}]^{\frac{1}{2}} [\overline{S}]^{\frac{1}{2}} \left\{ \begin{matrix} L_2 & L & \overline{L} \\ n\ell_1 & \ell_{1n} & L_1 \end{matrix} \right\} \left\{ \begin{matrix} S_2 & S & \overline{S} \\ s & s & S_1 \end{matrix} \right\}$$

$$\times \int_0^\infty f_\ell(r) f_{n\ell_1}(r) \, dr \times \left[\int_0^\infty f_\ell(r') f_{\ell_{1n}}(r') \, dr \right]^{N-2}$$

$$\times \int_0^\infty f_{n\ell_1}(r'')f_{m\ell_3}(r'') \, dr'' \times \left[\int_0^\infty f_{\ell_{1n}}(r) f_{\ell_{3m}}(r)dr \right]^{N-3} \right\}^2$$

$$Q^\dagger(E) Q^\dagger_{\ell_{1n}}(E') \quad .$$

There $Q^\dagger_{\ell_{1n}}(E)$ is the cross section for removing an electron from the core of the singly ionized excited state of the $(\ell_{1n}^{N-2}, n\ell_1)$ configuration. This cross section is proportional to the square-absolute value of the overlap integrals in Eq. (7c) between bound and the free electrons. Table V gives the overlap integrals for the bound atomic states of Eq. (7c) for neon, argon, and krypton and Tables VI and VII gives the necessary coefficients of fractional parentage for the p^N shells of the Noble gas atoms.

For the case of Noble gas atoms, we can also determine the possible $\overline{\phi}$ states in Eq. (7a) L=1, S=1/2, ϕ_2 is either [4]S, [2]P or [2]D. From the triangular relations of the 6-j symbols $\overline{\phi}$ can be [3]P when $\phi_2 = $[4]S, [1,3][S, P, D] when $\phi_2 = $[2]P and finally $\overline{\phi} = $[1,3][P, D], when $\phi_2 = $[2]D.

III. CONCLUSIONS

Two cases of excitation have been discussed. For case one, since the double ionization cross section is large[11], i.e., of the order of 10^{-17} cm^2 and because of the relatively large overlap integrals, we notice that removing two electrons from the valence shell causes an electron to go to an excited $n\ell''$ shell with a relatively high probability. From Table I we see that this probability decreases as n increases.

The probability of the excited electron to go to continum, that is to say the atom to be triply ionized, after the removal of two electrons, would be $(1 - \sum_n$ probability to go to $n\ell''$ excited shell). For the case of neon, we have $Q^{+++}(E) = 0.17 \ Q^{+++}(E)$, for argon $Q^{+++}(E) = 0.045 \ Q^{+++}(E)$ and for krypton $Q^{+++}(E) = 0.04 \ Q^{++}(E)$. Q^{+++} is the cross section for triply ionizing the atom. It is seen that in the measurements of ionization cross section of removing two electrons could possibly cause the atom to be rather triply ionized.

For case two, we treated two special situations. Both of these situations are not likely to occur in discharges of Noble gas atoms since the lifetime of the lower excited states are relatively short; however, in atoms where the excited states have longer lifetimes this situation could become probable. An example is the $3p^4[3p]-3d^2$ F states of argon. In this case, the atom becomes ionized and excited and then relaxes to the above ionized metastable state. If the population of these states is large, then it is quite possible that the atom becomes doubly ionized through these states. Labuda, et. al.[12], have measured the population density of these states and found them to be quite large.

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TABLE I

OVERLAP INTEGRALS FOR BOUND STATES FOR THE PROCESS $\ell^N \to \ell_n^{N-3}$, $n\ell_1$ FOR NOBLE GAS ATOMS $N=6$ AND n IS THE PRINCIPLE QUANTUM NUMBER OF THE EXCITED ELECTRON ℓ, ℓ_n and $n\ell_1$ ARE ALL p-ELECTRONS

$$\left[\int_0^\infty f_\ell(r)\, f_{\ell n}(r)\right]^3 \quad x \quad \int_0^\infty f_\ell(r)\, f_{n\ell}(r)\, dr$$

n	2	3	4	5	6	7	8
Neon	0.8888	-0.1904	-0.0553	-0.0266	-0.0166		
Argon		0.9612	-0.1723	-0.0460	-0.0222	-0.0133	
Krypton			0.9641	-0.1671	-0.0444	-0.0213	-0.0126

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TABLE II
EXCITATION CROSS SECTION FOR $|p^3 \phi_2, 4p\phi_1 \rangle$ STATES OF ARGON^{++} FOR CASE ONE AT ELECTRON ENERGIES OF ABOUT 100 EV.

$Q^{++}(100 \text{ ev}) = 2.96 \times 10^{-17} \text{ cm}^2$ (ref 10)

$$Q(|(3p^3)\, ^4S, 4p, \, ^1D_2 \rangle) = 2.17 \times 10^{-19} \quad cm^2$$

$$Q(|(3p^3)\, ^4S, 4p, \, ^3P_2 \rangle) = 0.95 \times 10^{-19} \quad cm^2$$

$$Q(|(3p^3)\, ^4S, 4p, \, ^3P_1 \rangle) = 0.57 \times 10^{-19} \quad cm^2$$

$$Q(|(3p^3)\, ^4S, 4p, \, ^3P_0 \rangle) = 0.19 \times 10^{-19} \quad cm^2$$

$$Q(|(3p^3)\, ^2D, 4p, \, ^3P_2 \rangle) = 1.20 \times 10^{-19} \quad cm^2$$

$$Q(|(3p^3)\, ^2D, 4p, \, ^3P_1 \rangle) = 0.72 \times 10^{-19} \quad cm^2$$

$$Q(|(3p^3)\, ^2D, 4p, \, ^3P_0 \rangle) = 0.25 \times 10^{-19} \quad cm^2$$

$$Q(|(3p^3)\, ^2P, 4p, \, ^1D_2 \rangle) = 0.72 \times 10^{-19} \quad cm^2$$

$$Q(|(3p^3)\, ^2P, 4p, \, ^3P_2 \rangle) = 0.72 \times 10^{-19} \quad cm^2$$

$$Q(|(3p^3)\, ^2P, 4p), \, ^3P_1 \rangle) = 0.42 \times 10^{-19} \quad cm^2$$

$$Q(|(3p^3)\, ^2P, 4p, \, ^3P_0 \rangle) = 0.13 \times 10^{-19} \quad cm^2$$

$$Q(|(3p^3)\, ^2P, 4p, \, ^1S_0 \rangle) = 0.57 \times 10^{-19} \quad cm^2$$

TABLE III

OVERLAP INTEGRALS FOR THE PROCESS $\ell^N \rightarrow \ell_{\ell n}^{N-2}, n\ell_1$

$$[\int_0^\infty f_\ell(r) f_{\ell n}(r)\, dr]^4 \times \int_0^\infty f_\ell(r)\, f_{n\ell_1}(r)\, dr$$

	a_2	a_3	a_4	a_5	a_6	a_7
Neon	0.980	-0.1308	-0.0525	-0.0290		
Argon		0.985	-0.1195	-0.0466	-0.0247	
Krypton			0.985	-0.1165	-0.04515	-0.0237

TABLE IV
OVERLAP INTEGRAL FOR THE CASE
$$(\ell_{1n}^{N-2}, n\ell_1) \rightarrow \ell_{1n}^{N-2} \rightarrow \ell_{2m}^{N-3}, n\ell_2$$

$$\left[\int_0^\infty f_{\ell_2 m}(r)\, f_{\ell_1 n}(r)\, dr \right]^3 \times \int_0^\infty f_{\ell_1 n}(r)\, f_{m\ell_2}(r)\, dr$$

Ne II / NeIII	$2p^3 - 2p$	$2p^3 - 3p$	$2p^3 - 4p$	$2p^3 - 5p$	$2p^3 - 6p$
$2p^4 - 2p$	0.9894	-0.1177	-0.0452	-0.0247	-0.0153
$2p^4 - 3p$	0.9996	-0.0476	-0.0227	-0.0133	-0.0088
$2p^4 - 4p$	0.9992	-0.0416	-0.0213	-0.0128	-0.0086
$2p^4 - 5p$	0.9992	-0.0397	-0.0209	-0.0127	-0.0085
$2p^4 - 6p$	0.9992	-0.0390	-0.0207	-0.0126	-0.0085

ArII / ArIII	$3p^3 - 3p$	$3p^3 - 4p$	$3p^3 - 5p$	$3p^3 - 6p$	$3p^3 - 7p$
$3p^4 - 3p$	0.9912	-0.1072	-0.0398	-0.0208	-0.0130
$3p^4 - 4p$	0.9996	-0.0435	-0.0205	-0.0116	-0.0075
$3p^4 - 5p$	0.9992	-0.0350	-0.0190	-0.0113	-0.0074
$3p^4 - 6p$	0.9992	-0.0323	-0.0184	-0.0111	-0.0074
$3p^4 - 7p$	0.9988	-0.0311	-0.0182	-0.0111	-0.0074

KrII / KrIII	$4p^3 - 4p$	$4p^3 - 5p$	$4p^3 - 6p$	$4p^3 - 7p$	$4p^3 - 8p$
$4p^4 - 4p$	0.9980	-0.1035	-0.0384	-0.0201	-0.0123
$4p^4 - 5p$	0.9996	-0.0417	-0.0198	-0.0112	-0.0071
$4p^4 - 6p$	0.9992	-0.0329	-0.0182	-0.0108	-0.0071
$4p^4 - 7p$	0.9988	-0.0297	-0.0176	-0.0107	-0.0071
$4p^4 - 8p$	0.9988	-0.0284	-0.0173	-0.0107	-0.0071

TABLE V
OVERLAP INTEGRALS FOR THE CASE
$$(\ell_{1n}^{N-2}, n\ell_1) \rightarrow (\ell_{1n}^{N-3}, n\ell_1) \rightarrow (\ell_{3m}^{N-3}, m\ell_3)$$

$$\int_0^\infty f_{\ell_1 n}(r)\, f_{\ell_3 m}(r)\, dr \;^3 \times \int_0^\infty f_{n\ell_1}(r)\, f_{m\ell_3}(r)\, d\sigma$$

NeII \ NeIII	$2p^3$-$2p$	$2p^3$-$3p$	$2p^3$-$4p$	$2p^3$-$5p$	$2p^3$-$6p$
$2p^4$-$2p$	0.9894	-0.1177	-0.0452	-0.0247	-0.0153
$2p^4$-$3p$	--	0.9341	-0.3680	-0.0842	-0.0477
-$2p^4$-$4p$	--	--	0.8134	-0.5405	-0.0704
$2p^4$-$5p$	--	--	--	0.6378	-0.7021
$2p^4$-$6p$	--	--	--	--	0.4223

ArII \ ArIII	$2p^3$-$3p$	$2p^3$-$4p$	$2p^3$-$5p$	$2p^3$-$6p$	$2p^3$-$7p$
$3p^4$-$3p$	0.9912	-0.1072	-0.0398	-0.0208	-0.0130
$3p^4$-$4p$	--	.9477	- .3402	-0.0768	-0.0438
$3p^4$-$5p$	--	--	.8444	-0.5102	-0.0653
$3p^4$-$6p$	--	--	--	0.6828	-0.664
$3p^4$-$7p$	--	--	--	--	0.4702

KrII \ KrIII	$4p^3$-$4p$	$4p^3$-$5p$	$4p^3$-$6p$	$4p^3$-$7p$	$4p^3$-$8p$
$4p^4$-$4p$	0.9920	-0.1035	- .0389	-0.0201	-0.0123
$4p^4$-$5p$	--	0.9555	-0.3329	-0.0742	-0.0425
$4p^4$-$6p$	--	--	0.8527	-0.4794	-0.0634
$4p^4$-$7p$	--	--	--	0.6954	-0.6557
$4p^4$-$8p$	--	--	--	--	0.4919

TABLE VI

COEFFICIENTS OF FRACTIONAL PARENTAGE
FOR STATES $p^5 \phi$ WITH $p^4 \phi_1$ PARENTS

$p^5 \phi / p^4 \phi_1$	^1S	^3P	^1D
^2P	$\sqrt{\dfrac{1}{15}}$	$\sqrt{\dfrac{3}{5}}$	$\sqrt{\dfrac{1}{3}}$

TABLE VII

COEFFICIENTS OF FRACTIONAL PARENTAGE
FOR STATES $p^4 \phi_1$ WITH $p^3 \phi_2$ PARENTS

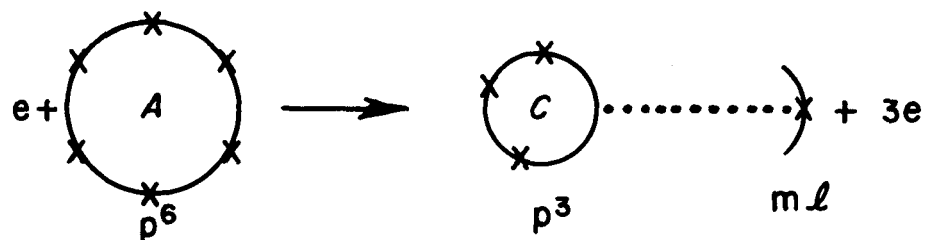| $p^4 \phi_1 / p^3 \phi_3$	^4S	^2P	^2D
^3P	$\sqrt{\dfrac{1}{3}}$	$-\dfrac{1}{2}$	$-\dfrac{1}{2}\sqrt{\dfrac{S}{3}}$
^1D		$-\dfrac{1}{2}$	$\sqrt{\dfrac{3}{2}}$
^1S		1	

Fig. 1. An electron colliding with a neutral Noble gas atom resulting in three free electrons and an excited doubly ionized atom. For argon if the colliding electron has a kinetic energy of 100 ev the cross section for the $3p^3$-4p configuration is 8.9×10^{-19} cm^2.
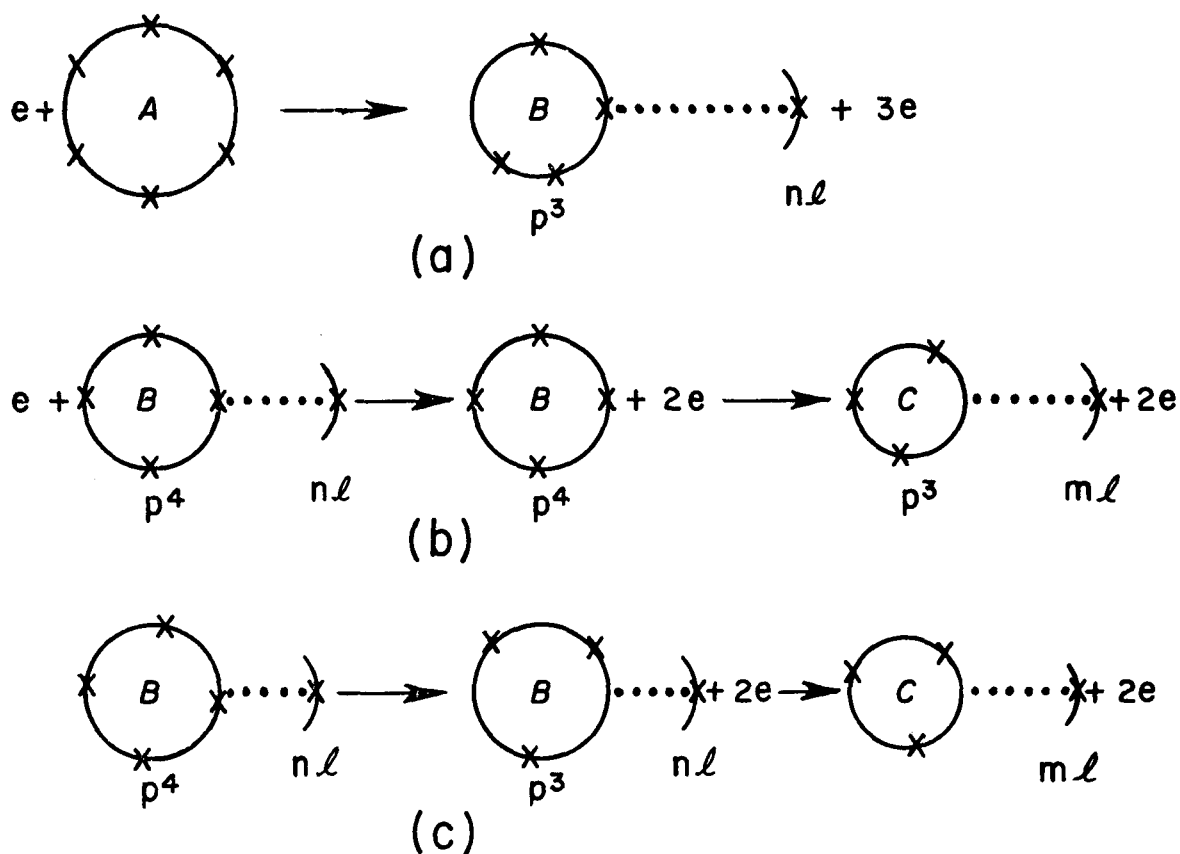
Fig. 2. Here the process of excitation is in two steps.

(a) The atom loses an electron and becomes
excited to a p^4-$n\ell$ configuration.

(b) The excited ionized atom makes another
collision, loses its excited electron
and then relaxes to a doubly ionized
excited state.

(c) The excited ionized atom through collision
loses one of its core electrons and
then relaxes to a doubly ionized
excited state.