Relative Abundance of Ions Yield
as the Result of 1s and 2p Shell Ionization
in Potassium and Calcium Atoms

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Abstract

Relative abundance of charged ions and mean charged ions are calculated following 1s and 2p vacancy production in potassium and calcium atoms. The calculations are performed with Monte Carlo simulation method. The simulation based on the tracing of all possible radiation, non-radiation transitions and electron shake off probabilities after inner shell vacancy creation. The radiative transition rates and electron shakes off processes are obtained with Multiconfiguration-Dirac-Fock (MCDF) wave functions model. The non-radiation transition rates are carried out using Dirac-Fock-Slater (DFS) wave functions. At 1s hole states in Potassium atom, the yield of $K^{5+}$ ions are the prominent produces. The doubly charged $K^{2+}$ ions predominate over $K^{3+}$ ions after 2p shell ionization in potassium. On the other hand, the $Ca^{3+}$ ions dominate over $Ca^{2+}$ ions in Calcium. The considerations of closing some Coster-Kronig channels and electron shake off processes through the simulation improve the results of charged ions with the experimental data. The results of electron shake off probabilities are compared with other theoretical calculation. The results of relative abundance of charged ions agree well with the experimental data.
1 - Introduction

The relaxation of inner-shell ionized atom starts by filling the initially vacancy either by a radiative transition (x-ray) or by non-radiative transition (Auger and Coster-Kronig). New vacancies created during this atomic reorganization may, in turn, be filled by further subsequent radiative and non-radiative transitions until all vacancies reach the outermost occupied shells. In the case of radiative transition the vacancy moves to an outer shell under emission of characteristic x-rays, while for non-radiative transitions one electron from an outer shell fills up the inner-shell vacancy and another electron is ejected into the continuum. For example, $1s \, 2s^2 \, 2p^6$ would represent a distribution with a single K-shell vacancy ($N=1$); $1s^2 \, 2s^2 \, 2p^5$. would represent a distribution that could be formed the initial distribution by radiative decay ($N=1$), and $1s^2 \, 2s \, 2p^5$. Would represent a distribution that could be formed via an Auger transition ($N=2$). The electron shake off processes occurring due to the change of atomic potential after primary ionization or after Auger and Coster-Kronig transitions. The shake off process produces additional vacancies in the higher shells leading to an increase in the number of vacancies in the atomic levels. The generation of vacancies in the course of vacancy cascade is accompanied by characteristic energy shifts in the atomic levels. The influence of the additional vacancies during the cascades may close some low-energy Coster-Kronig channels (forbidden energies). Understanding the influence of the additional vacancies on the Auger and Coster-Kronig transitions, gives more detailed information about the vacancy cascade development. The overlapping radiative and non-radiative spectra emitted from parallel branches of the vacancy cascades lead to different low-energy highly charged ions. There is currently considerable interest in low-energy highly charged ions for the study of collision processes common in laboratory and astrophysics, for use in precision spectroscopic tests of quantum electrodynamics, and for the test of quantum mechanical theories of electron transfer. The charge-state distributions of ions of argon and potassium following X-ray absorption at energies near their respective K-edges are measured using time-of-flight techniques [1]. Matsuo et al. [2] measured the charge state distribution of photoions from K and Ca targets in the L shell ionization region (270-400 eV for K, 330-500 eV for Ca) using a time-of-flight technique occupied with synchrotron radiation. Branching ratios of multiply charged ions formed through photoionization of Kr 3d,3p and 3s sub-shell are measured using a coincidence technique by Tamenori et
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al. [3]. Yield spectra of the multiply charged ions $Kr^{2+}$, $Kr^{3+}$, $Kr^{4+}$ and $Kr^{5+}$ in coincidence with threshold have been measured near the 3p-shell ionization region of Kr atoms [4]. Multiple ionization of Ne, Ar, Kr and Xe atoms are measured using 1.0 MeV/emu $H_2^+$ projectiles for both breakup and nonbreakup channels [5]. The cascade decay of atomic magnesium after photoionization with a photoelectron-photoion coincidence method on the 1s, 2s, and 2p decay are investigated by Kannegießer et al. [6]. Auger cascade processes following the Kr $3d_{5/2} \rightarrow 5p$ and Xe $4d_{5/2} \rightarrow 6p$ excitations studied both theoretically and experimentally by Muttila et al. [7]. Jens Viefhaus et al. [8] studied the relaxation processes after non-resonant inner-shell photoionization of Kr and Xe atoms using electron-electron time-of-flight coincidence spectroscopy. The 3d photoionization and subsequent normal Auger decay processes in atomic strontium are theoretically investigated using multiconfiguration Dirac-Fock method by Nikkinen et al. [9]. The charge spectra of multiply ions resulting from vacancy cascades in Ne, Ar, Kr and Xe atoms are calculated by straightforward construction of de-excitation trees originating from various initial inner-shell vacancies Kochur et al. [10]. Omar and Hahn [11,12] applied the radiative and Auger emission in cascade (RAC) model to the calculation of the final-charge-state distribution in the decay of $Ar^{+}(1s)$ with an initial 1s hole created by synchrotron irradiation. The decay of inner-shell vacancy in atoms through radiative and non-radiative transitions is calculated using Monte-Carlo simulation method [13–16]. The electron shakes off probabilities of atoms as a result of vacancy production are calculated in the sudden approximation using the Hartree-Fock-Slater (HFS) wave functions [17–19].

In the present work Monte-Carlo simulation technique is applied to calculate the ion-charge state distributions and average atomic charged ions produced following 1s and 2p subshell vacancy creation in potassium and following 2p vacancy production calcium atoms, respectively. All allowed radiative, non-radiative branching ratios and electron shake off probabilities are taken into account in the calculation of the atomic reorganization. The radiative transition rates and electron shakes off processes are obtained with Multiconfiguration-Dirac-Fock (MCDF) wave functions model [20]. The non-radiative transition rates are carried out with Dirac-Fock-Slater (DFS) wave functions from [21]. The change of x-ray, Auger and Coster-Kronig transition rates and transition energies are carried out using scaling procedure method. The forbidden Coster-Kronig channels are considered and excluded during the vacancy cascade simulation. The results electron shake off probabilities are compared
with other theoretical calculation. The relative abundance of charged ions result following K and L\textsubscript{23} vacancy creation in potassium and calcium atoms are compared with experimental values.

2 - Method of calculation

A Monte-Carlo technique is applied to simulating vacancy cascades following L\textsubscript{23} inner-shell vacancy decay of K and Ca atoms considering x-ray emission, Auger and Coster-Kronig transitions and electron shake off processes. The only attempt to obtain a systematic solution of the complete atomic reorganization following inner shell vacancy creation in atoms is the Monte Carlo calculation method. The description of the cascade decay after inner-shell vacancy creation is discussed in detail in the following section. An analysis of each cascade starts with the implementation of atomic for all possible radiative, non-radiative transitions and electron shake off processes. To realize a Monte-Carlo selection of the actual decay channel, the probabilities of all de-excitation channels were normalized to one. Then a random number generated in the interval [0,1] selects the next de-excitation step including vacancy transfer and ionization. After creating a new vacancy in an actual subshell, the program controls at first whether shake off process takes place or not. If the random number generated is smaller than the sum of all normalized shake off probabilities of the preceding vacancy configuration, then a shake off process takes place. The channel whose subshell shake off probability value coincides with the random number generated will be activated. After the decision about the occurrence of shake off processes the program selects the following de-excitation channel by generating a new random number. Here at first a comparison of the value of the random number and the fluorescence yield proves whether radiative or non-radiative transitions take place. The actual de-excitation channel after this decision is chosen in analogy with the determination of the shake off channels. For each new hole the program code goes back to the first step described above. The generation of new vacancy configurations continues until all vacancies have reached the outer shell atom. Then the number of vacancies is recorded. After finishing off a cascade will be simulated again. After $10^5$ histories the ion charge state distributions and the average charged ions are produced. The calculation method employed by making a random selection of the possible radiative and non-radiative transitions from a table of weighted probabilities. The radiative
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transition rates can be calculated using time-dependent perturbation theory:

\[ \Gamma_{i \rightarrow f}(r \rightarrow i) = \left( \frac{4\omega^3}{3hc^3} \right) \left( \frac{1}{2J+1} \right) |\langle \psi_f | D | \psi_i \rangle|^2 \]  

(1)

where \( \psi_i \) is the initial state, \( \psi_f \) is the final state of the system, is the angular frequency, \( c \) is the speed of light and \( D \) is the electric dipole operator. The Auger transition rates are given by:

\[ \Gamma_{i \rightarrow f}^A(r \rightarrow i) = \left( \frac{2\pi}{\hbar} \right) \Sigma |\langle \psi_f | H^* | \psi_i \rangle|^2 \rho(\varepsilon) \]

(2)

where Hee is the operator of the electron-electron interaction. The density of final state \( \rho(\varepsilon) \) is unity when the continuum-state wave function is normalized in the energy scale. The \( \Sigma \) denotes the average of the sum over the initial and the final states. The radiative and non-radiative branching ratios are defined as the probability that the vacancy in an atom is filled through x-ray transitions (photon emission) or through Auger and Coster-Kronig processes and are given by: for fluorescence yield;

\[ \omega(f \rightarrow i) = \left( \frac{\Gamma_{i \rightarrow f}^R}{\Gamma} \right) \]

(3)

and for Auger yield;

\[ a(f \rightarrow i) = \left( \frac{\Gamma_{i \rightarrow f}^A}{\Gamma} \right) \]

(4)

where \( i \) is the initial configuration decaying into the final configuration \( f \). is the sum of partial radiative widths and non-radiative width and is given by:

\[ \Gamma = \sum_{i,f} \Gamma_{i \rightarrow f}^R + \sum_{i,f} \Gamma_{i \rightarrow f}^A \]

(5)

The calculations of radiative transition rates are performed for singly ionized atoms using Multiconfiguration-Dirac-Fock (MCDF) wave functions. The non-radiative transition rates are computed using Dirac-Fock-Slater (DFS) wave functions.

The electron shake-off process resulting from the sudden change of the atomic potential during vacancy cascade development, which can lead to the ejection of additional electrons through the atomic reorganization processes are calculated. In this way we calculate the electron shake-off probabilities according to Aberg [22] by overlapping integrals between the wave functions.
of initial state $\varphi(1)$ and the final state of the considered process. The probability of an electron transition from the orbital $nlj$ to the orbital $n'l'j'$ is given by

$$p_{nlj \rightarrow n'l'j'} = |\int \phi_{nlj}^*(A_0)\phi_{nlj}(A) d\tau|^2$$

with $\varphi_{nlj}(A)$ and $\varphi_{n'l'j'}(A_0)$ being orbital wave functions for the orbital $nlj$ and for the orbital $n'l'j'$ in the ion $A_0$. Thereby the ion originates from the atom $A$ by a change in the potential in the course of the ionization processes. The probability that at least one of the $N$ electrons located in the subshell becomes ionized is given by

$$p = 1 - \frac{1}{N} \left( |\int \phi_{nlj}^*(A_0)\phi_{n'l'j'}(A) d\tau|^2 \right)^N - p_f$$

where the quantity $p_f$ represents a correction for physically not allowed transitions to occupied shells and has the form

$$p_f = \sum_{n'lj} N \frac{N'}{2j+1} \left| \int \phi_{n'lj}^*(A_0)\phi_{nlj}(A) d\tau \right|^2$$

with $n' \neq n$ and $N$ is the number of the electrons in the orbital $n'lj$. The creation of multiple vacancies causes photon energy shifts and may result in an energetic closing of the channel for certain Coster-Kronig transitions. In the determination of the population of the multiple vacancy states, the vacancy cascade modeling takes into account the fact that the change of radiative and non-radiative transition rates occurs due to transition energy shifts. The correction of the transition rates quantum-mechanically requires more difficult calculations. Therefore the transition rates are calculated according to the following scheme. At first quantum mechanically determined transition rates are calculated for singly ionized atoms. The corrected transition rates for multiply ionized atoms are carried out using the following relationships [23]:

The radiative transition rates for multi-ionized atoms are given by:

$$a_r(n_1l_1^{N_1}, n_2l_2^{N_2} \rightarrow n_1l_1^{N_1-1}, n_2l_2^{N_2+1}) = N_1 \frac{4l_2 + 2 - N_2}{4l_2 + 2} A_r(n_1l_1 \rightarrow n_2l_2)$$

and the non-radiative transition rates are given by:

$$a_a(n_1l_1^{N_1}, n_3l_3^{N_3}, n_4l_4^{N_4} \rightarrow n_1l_1^{N_1-1}, n_3l_3^{N_3+1}, n_4l_4^{N_4+1}) =$$

$$N_1 \frac{(4l_3 + 2 - N_3)(4l_4 + 2 - N_4)}{(4l_3 + 2)(4l_4 + 2)} A_a(n_1l_1 \rightarrow n_3l_3, n_4l_4)$$
If both of the final vacancies occur in the same principle shell, the non-radiative transition rates are given:

\[
a_a(n_1i_1^{N_1}, n_3i_3^{N_3}) \rightarrow n_1i_1^{N_1-1}, n_3i_3^{N_3+2}) = \\
\frac{N_1}{2} \frac{(4l_3 + 2 - N_3)(4l_3 + 1 - N_3)}{(4l_3 + 1)} A_a(n_1i_1 \rightarrow n_3i_3^2)
\]  

(11)

where \(A_r\) and \(A_a\) are the radiative and non-radiative transition rates for single ionized atom, respectively, \(ar\) and \(aa\) are the transition rates for atom with various spectator inner-shell vacancies, \(n_1i_1\) is initial state and \(n_3i_3, n_4i_4\) are a the final state, and \(N_i\) is the number of vacancies in the \(n_i l_i\) sub-shell.

3 - Results and Discussions

The electron shake off probabilities accompanying formation of 1s and 2p vacancies are computed for K and Ca atoms. The calculations of shake off probabilities are obtained Multiconfiguration-Dirac-Fock (MCDF) wave functions [20]. The calculated results for shake off probabilities from various shells as the result of 1s and 2p in K and Ca are plotted in figures 1, 2. It is found that, the shake off probabilities increase with increasing orbital quantum number \((l)\) in atoms. The probability is higher in \(N_1, M_{23}, M_1\) and \(L_{23}\) in both K and Ca atoms after K-shell ionization, respectively. The importance of this shake process encourages us to consider it in the calculation of the ion charge state distributions. Comparison with other theoretical calculation [18] is made.

The influence of the additional vacancies after the electron emission may close some low-energy Coster-Kronig channels. Figure 3 shows a closing of energetically forbidden \(L_1 - L_{23}M_1\), \(L_1 - L_{23}M_{23}\) and \(L_1 - L_{23}N_1\) Coster-Kronig channels in K and Ca during vacancy cascade population after K-shell ionization. The \(L_1 - L_{23}M_1\) Coster-Kronig channel became forbidden after two vacancies production for both inner-shell ionized K and Ca atoms, whereas the \(L_1 - L_{23}M_{23}\) channel is closed after three vacancies generation. The \(L_1 - L_{23}N_1\) Coster-Kronig channel in inner-shell ionized K atom is closed after one vacancy creation during the de-excitation cascade, whereas this channel closed after two vacancy creation in the case of Ca atoms. Not considering the energetic shell structure leads to a deformation in the ion charge spectrum in the comparison with the experimental spectra. Monte-Carlo method is performed on the basis of radiative, non-radiative branching ratios and electron shake off processes.
for single ionized K and Ca atoms. The radiative and non-radiative branching ratios for possible transitions in K and Ca atoms are calculated using Multiconfiguration-Dirac-Fock (MCDF) wave functions and Dirac-Fock-Slater wave functions, respectively. The radiative branching ratios were calculated from equation (3) and the non-radiative branching ratios from equation (4). During the vacancy cascade development the electron emission is accompanied with energy shifts in the atomic levels. Figure 4 shows the calculation of the relative abundances of charged ions resulting from atomic reorganization after 1s\(^{1+}\) vacancy production in potassium atoms. The calculation is made with and without consideration the electron shake off process during the 1s\(^{1+}\) vacancy de-excitation. This process occurs from primary ionization and from Auger transitions in the course of de-excitation cascades. The electron shake-off process leads to additional holes in the outer shell of atom. It is found that, the electron shake off process lead to increase the number of vacancies in the atom through the vacancy cascade development. The importance of shake off processes is demonstrated in the figure. The consideration of electron shake off processes in the calculation of de-excitation cascades improves the results of the charged ions with the experimental data [1]. The ion charge state distributions are normalized to the total abundances of 1.0. At 1s hole state in K, the probability of fluorescence yield is lower than the Auger and Coster-Kronig yield. The fluorescence yield will occur in lower 1% whereas the Auger and Coster-Kronig yield is above 99%. The K2+ ions are formed from \(L_{23}\) hole and subsequent \(L_{23}-MN\) Auger transitions. The \(L_{23}\) hole is generated after filling K-shell vacancy via fluorescence. The 1s ionization followed by K-\(L_{23}M\) Auger transition leads to \(K^{3+}\) ions. The de-excitation pathway after K-shell ionization is K-\(L_{23}M, L_{23}[M]-MN[M]\), this cascade leading to a stable \(M^{-2}\) and \(N-1\) hole state (\(K^{3+}\)). The subsequent of K-\(L_{23}\) \(L_{23}\) gives rise to final \(K^{4+}\) ions. The de-excitation pathway of 1s shell hole is the successive K-\(L_{23}L_{23}, L_{23}[L_{23}]-MM[L_{23}], L_{23}[M^2]-MN[M^2]\). The \(K^{5+}\) ions arise from subsequent K-\(L_{23}L_{23}\) transition and from shake-off process. The de-excitation of 1s holes leads to production of \(K^{n+}\) (\(n = 2 - 7\)) ions for potassium. The 1s hole transferred via K-\(L_1L_1\) Auger transition, and subsequent \(L_1[L_1]-L_{23}M[L_1], L_1[L_{23}M]-L_{23}M[L_{23}M], L_{23}[L_{23}M_2]-MM[L_{23}M_2], L_{23}[M_4]-MN[M_4]\). This branching gives rise to stable \(M^{-5}\) \(N^{-1}\) hole state \(K^{6+}\) ions. The \(K^{5+}\) and \(K^{4+}\) ions are predominate after 1s vacancy production in potassium atoms. The results agree well with the experimental data [1]. The relative abundances of charged ions formed as result of 2p vacancy in K and Ca atoms are illustrated
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in figure 5. The de-excitation of core hole in K and Ca gives rise to different ionic charges. Each branch of the de-excitation leads to an ion of a specific charge. The relaxation of ionized atom occurs through radiative and/or non-radiative transitions and electron shake off probabilities. The 2p ionization followed by $L_{23}$ -MN Auger transition leads to $K^{2+}$ ions in potassium atom, whereas the $Ca^{2+}$ ions formed from the $L_{23}$-NN Auger transition. The $K^{q+}$ ($q=3,4$) ions yield through de-excitation decay $L_{23}$-MN Auger transitions and electron shake off processes. At 2p hole state in potassium atom, the $K^{2+}$ ions are predominate, whereas the $Ca^{3+}$ ions dominate after 2p shell ionization in calcium atoms. The results agree well with the experimental values [2].

4 - Conclusions

Monte-Carlo simulation technique is applied to calculate the ion-charge state distributions and average atomic charged ions produced following inner shell vacancy creation in potassium and calcium atoms. All allowed radiative, non-radiative branching ratios and electron shake off probabilities are taken into account in the calculation of relative abundances of charged ions. The radiative transition rates and electron shakes off processes are obtained with Multiconfiguration-Dirac-Fock (MCDF) wave functions. The non-radiative transition rates are carried out with Dirac-Fock-Slater (DFS) wave functions. The forbidden Coster-Kronig channels and electron shake off processes are considered in the calculation of the relative abundances of charged ions. Not considering the closing of forbidden Coster-Kronig channel and electron shake off probabilities through the vacancy cascades population leads to deformation in the relative abundances of charged ions in comparison with the experimental values. The results agree well with the expriment.

References


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Figure 1: Electron shake off probabilities result from 1s vacancy production in K and Ca atoms.
Figure 2: Off probabilities after L23 subshell vacancy production in K and Ca.
Figure 3: Closing of some Coster-Kronig channels after emission of various electrons during vacancy cascade propagation in K and Ca atoms.
Figure 4: Comparison of relative abundances of ions calculated with and without consideration of shake off process result after 1s vacancy production in potassium atom with experimental data [1].
Figure 5: Ion charge state distributions result from 2p shell ionization in K and Ca atoms. The average charged ions is given in the upper right hand corner.