L-Subshell Ionization Cross Sections for Hf, Ta and W by H\(^+\) and He\(^+\) Bombardment


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ABSTRACT. X-rays resulting from L-subshell vacancies in Hf, Ta and W produced by bombarding thin targets with H⁺ (0.6 - 2.5 MeV) and He⁺ (1.2 - 4.2 MeV) were detected by Si(Li) spectrometry. Ionization cross sections were obtained by using the above measurements, branching ratios from theoretical calculations and values of the fluorescence yields and Coster-Kronig factors obtained by interpolating from experimental data. The observed projectile energy dependence of the L₁⁺ subshell ionization cross section is reasonably well reproduced by the plane wave Born approximation (PWBA) but the introduction of relativistic, trajectory and binding corrections (PWBA-BTR) are essential for the description of the L₁ and L₁II data. Scaling of the H⁺ and He⁺ data shows good agreement one with the other. The behavior of the ionization cross section versus bombarding energy is correlated with some special features of the electronic bound-state wave functions.

RESUMO. Feixes de H⁺ e He⁺ com energias entre 0,6 e 2,5 MeV, obtidos com o acelerador Van de Graaff da PUC/RJ, foram usados para produzir vacâncias nas camadas L do Hf, Ta e W. Os raios X emitidos foram detectados com um detector de Si(Li) e analisados em energia e intensidade. Esses dados, as razões de ramificação calculadas teoricamente, os coeficientes de fluorescência e fatores Coster-Kronig obtidos por interpolações de dados experimentais foram utilizados na determinação das seções de choque de ionização para esses elementos.

A dependência da seção de choque de ionização com a energia do projétil é razoavelmente bem descrita pela aproximação de Born(PWBA) no caso das subcamadas L₁. No entanto, a introdução de correções tais como relativística, de trajetória e de energia de ligação são necessárias na descrição das seções de choque de ionização das subcamadas L₁ e L₁II(PWBA-BTR).

Os resultados relativos à ionização com os feixes de H⁺ e He⁺, quando normalizados, são concordantes.

Um dos aspectos importantes observados é a correlação entre a variação da seção de choque de ionização com a energia do feixe incidente e as funções de distribuição eletrônicas dos estados ligados do alvo.

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1. INTRODUCTION

In the past few years much progress has been made in the study of inner-shell vacancy production. We have recently measured the L-subshell ionization cross sections of Au, Pb, Bi, Th and U by proton impact. In that work, it was observed that the general trend of experimental points of the ratios of the ionization cross sections \( \sigma_{I}^{L_2} / \sigma_{I}^{L_1} \) and \( \sigma_{I}^{L_3} / \sigma_{I}^{L_1} \) is the same as that exhibited by PWBA calculations. However, in general, the position of the maximum obtained in PWBA calculations is shifted toward energies higher than the experimental values and the theoretical curves are displaced upwards.

These features became evident since the first detailed analysis of the energy dependence of the L-subshell ionization cross sections (see, for instance, ref. 2).

The available tabulated PWBA calculations make use of non relativistic hydrogenic wave functions. It is noteworthy that the 2s density nodes from Hartree-Fock calculations occur systematically nearer the origin than those obtained from hydrogenic wave functions. The shift corresponds to two or three units in the effective charge and thus would explain the shift in the position of the maximum in the ratio \( \sigma_{I}^{L_2} / \sigma_{I}^{L_1} \) and \( \sigma_{I}^{L_3} / \sigma_{I}^{L_2} \).

On the other hand, near the nucleus, relativistic wave functions are generally larger than non relativistic ones. Thus, the 2s state, with an electron density in the vicinity of the nucleus larger than that of the 2p states, is more affected by relativistic effects and the resultant
increase in $\sigma_I^{L_1}$ cross section must dominate those expected in $\sigma_I^{L_2}$ and $\sigma_I^{L_3}$. A reduction in the $\sigma_I^{L_2}/\sigma_I^{L_1}$ ratios would be a natural consequence of using relativistic wave functions.

The ionization cross section $\sigma_I^{L_1}$ showed, for all the heavy elements studied, a more or less pronounced knee in the region of proton energy just above 1 MeV. This inflection is predicted by the PWBA and it has been proposed that it could be explained in terms of the radial distribution of electron densities. In fact a correlation was observed between the density nodes and the dominant impact parameters obtained from the approximate position of the plateau in the $\sigma_I^{L_1}$ curves.

These facts suggest the possibility of obtaining deeper information about the bound-state electronic wave functions from the analysis of the behavior of the ionization cross sections versus incident energy curves.

The above results and comments led us to extend the measurements for intermediate heavy elements (Hf, Ta and W). Besides we looked also at all these effects in bombardment with He ions. In fact, in the frame of PWBA calculations, ionization cross-sections for H and He can be compared directly if a scaling of the incident energy is made.

The present work reports the results of a study of the projectile energy dependence of Hf, Ta and W I-subshell ionization cross sections for $H^+$ energies between 0.6 and 2.5 MeV and $He^+$ energies between 1.2 and 4.2 MeV. The
L-subshell ionization cross sections of Ir by protons in the same interval of energy was also measured.

2. EXPERIMENT

Beams of H\textsuperscript{+} and He\textsuperscript{+} were produced at the PUC/RJ Van de Graaff accelerator. The beam was directed onto targets placed at 45° with respect to its axis. Targets with a thickness of approximately 50 \( \mu \text{g/cm}^2 \) were prepared by vacuum evaporation of Hf, Ta and W onto thin formvar films. In all the cases, the thickness of the targets was small enough to avoid self-absorption of the x-rays and degradation of the beam energy within the target. They were monitored during each run by Rutherford scattering of the ions through 90°.

All the measurements were performed with a Si(Li) detector system (180 eV full width at half-maximum at 6.4 KeV). The detector was positioned at 90° with respect to the beam and was separated from the target by a 4 mm diameter Mylar window 6 \( \mu \text{m} \) thick.

The efficiency calibration procedure as well as further details of other experimental procedures and the method used in the analysis of the spectrum are given in Ref. 1. For the determination of x-rays production cross sections, the well defined lines \( \Lambda_{44/2} \), \( \Lambda_{55/2} \), \( \Lambda_{64/2} \), \( \Lambda_{75/2} \), \( \Lambda_{86/2} \) and \( \Lambda_{97/2} \) were used.
3. EXPERIMENTAL RESULTS

A - Measured x-ray production cross sections

The absolute k-line production cross section for thin targets is obtained from \( N_x^k \), the measured number of counts in the k-line, and is given by

\[
\sigma_x^k(E) = \left( \frac{d\sigma}{d\Omega} \right)_R \frac{N_x^k}{N_p} \frac{\Omega_p}{(1-\tau)\epsilon}
\]

at each incident energy \( E \). In the above expression, \( \tau \) and \( \epsilon \) are, respectively, the fractional dead time and the overall efficiency of the x-ray spectrometer at the energy of the k-line, \( (d\sigma/d\Omega)_R \) is the differential cross section for Rutherford scattering of particles (H\(^+\) or He\(^+\)) at 90\(^0\) laboratory angle, \( \Omega_p \) is the solid angle subtended by the particle detector and \( N_p \) is the number of particles scattered by the target element through the particle detector.

The numerical values of the measured x-ray production cross section for the selected lines, for H\(^+\) and He\(^+\), are available upon request. The errors come mainly from the x-ray detector efficiency curve; the statistical errors from counting are very small, except for \( \sigma_x^\alpha \).

To go from the directly measured x-ray production cross sections to the L\(_1\)-subshell ionization cross sections, relative radiative and non-radiative decay rates of each subshell are needed. In fact, the ionization cross sections can be written as explicit functions of the x-ray production cross section, as presented in Ref. 1. Contributions from...
K-shell primary vacancies to the L-shell x-ray yield are negligible.

The relative decay rates can be taken from Scofield\textsuperscript{7,8} or Rosner and Bhalla\textsuperscript{9}. In a previous work\textsuperscript{10}, we have observed that the experimental values obtained with a Si(Li) spectrometer seem almost as good as those obtained with crystal spectrometers. However, neither method allows clear-cut conclusions about the L x-ray emission rates. The best that could be said is that they follow the general trends predicted by relativistic Hartree-Fock-Slater calculations.

In the case of ionization produced by He\textsuperscript{+}, multiple ionization effects need to be investigated because the calculated values of the relative decay rates were not obtained in the general case where outer vacancies are present. On the other hand, the overall resolution of our experimental set-up does not allow the separation of possible satellite lines. A survey of the ratio of the x-ray production cross section for pairs of lines corresponding to the same initial state of the vacancy for different He\textsuperscript{+} energy was made. No significant modification of this ratio was observed, indicating that multiple ionization effects are not very important in the range of energies 1.2 - 4.2 MeV for He\textsuperscript{+} projectiles.

However, as observed in Ref. 10, satellite lines are always present. In fact, the transference of vacancies from the K to the L shell by Auger transition, and the internal redistribution of vacancies among the subshells by the Coster-Kronig process, create L-vacancies accompanied
by an external second vacancy, which modifies both the
energy and the transition rates for the radiative filling
of the L vacancy. The agreement between experimental values,
where the principal and satellite lines are not separated,
and theoretical calculations of the principal lines suggests
that the perturbation introduced by secondary outer vacancies
is unimportant, reinforcing the use of theoretical values
for the relative decay rates.

The values of the L-subshell fluorescence yields
and Coster-Kronig factors used in the present work were taken
from the compilation made by Šambynek et al. of available
experimental and theoretical values in our region of interest.
We interpolate from experimental data, always verifying the
normalization relations. These normalizations were always
satisfied better than 5%. The adopted values are given in
Table I.

Our values of the scaled ionization cross sections
\( \sigma_{L_i/Z_i}^{L_i} \) versus E/A are presented in Fig. 1, together with
the Xcode PWBA calculations. The relativistic correction
embodied in the PWBA-BTR curves is discussed in section IV.

Since most of the systematic errors involved in
the measurements of the x-ray yields can be eliminated by
working with cross section ratios, we present in Fig. 2 the
scaled results for the ratios \( \sigma_{I_{L_2}}^{L_2}/\sigma_{I_{L_1}}^{L_1}, \sigma_{I_{L_3}}^{L_3}/\sigma_{I_{L_1}}^{L_1} \) and \( \sigma_{I_{L_3}}^{L_3}/\sigma_{I_{L_2}}^{L_2} \).

4. DISCUSSION

Reasonable agreement was found between experimental
results and the plane wave Born approximation. However, a systematic tendency of the theoretical curves to be displaced downwards is clearly observed for the $L_i$ ionization cross section. It is worthwhile to emphasize that a possible poor choice of some of the relative decay rates does not affect the experimental points to an extent that will overcome the gap between them and the PWBA predictions.

It is usual to introduce corrections due to the changing binding energy of the target electrons in slow collisions and due to the deflection in the trajectory of the incident ions. As a matter of fact, the general agreement we found after introducing these corrections is worse since the overall result of this is a further reduction in the calculated values of the ionization cross sections. On the other hand, corrections due to the relativistic effects in the L-shell wave functions may increase significantly the calculated cross sections. The relativistic corrections are very lengthy to calculate if we begin by introducing the appropriate Dirac wave function in the Born matrix elements. There is an old crude prescription suggested by Hönl that permits, by an adequate change in the PWBA $\theta_{L_1}$ parameter (defined in Ref. 16), a simulation of the relativistic effects. In this procedure one continues to employ non-relativistic hydrogenic wave functions, but takes into account the modification of the ionization potential through a reduction in the $\theta_{L_1}$ parameter. It is, thus, somewhat equivalent to the usual binding energy correction since $\theta_{L_1}$ is proportional to the ratio of the true binding energy of the $L_1$ subshell to
that predicted by a hydrogenic wave function.

Combining binding, trajectory and relativistic effects, the PWBA-BTR curves in Figures 1 and 2 are obtained. A surprisingly good agreement was reached for the $L_1$ and $L_3$ cross sections. The relativistic correction is overestimated in the $L_2$ case. The reason for this is that the $j = 1/2$ states, either $l = 0$ or $l = 1$, are treated on equal footing in Hönl's recipe. For heavier elements, the relativistic bound-state wave functions are much larger than the non-relativistic ones near the nucleus and the $l = 0$ states are much more affected by the correction than the $l = 1$ states. The contribution to the transition matrix elements mainly arises from the region of large momentum transfer and this occurs for low incident energy in the vicinity of the nucleus. The final result is a significant increase in the $L_1$ ionization cross section at low bombarding energies, to a lesser extent in the $L_2$ case and an even smaller effect in the $L_3$ case.

Since the PWBA-BTR calculations are so successful for $L_1$ and $L_3$ subshells, an excellent agreement was found for the $\sigma_{L_3}/\sigma_{L_1}$ ratio. Ratios involving $\sigma_{L_2}$ are poorly described by these calculations. In the $\sigma_{L_3}/\sigma_{L_2}$ case, the PWBA and PWBA-BT curves coincide and the net effect exhibited by the PWBA-BTR curve is that related to the relativistic correction. The exaggerated correction introduced in $L_2$ is clearly revealed. However, the need for some relativistic correction in $\sigma_{L_2}$ greater than that of $\sigma_{L_3}$ is evident.

The scaling for $H^+$ and $He^+$ ions gives the predicted
results, but the energy of the He\(^+\) ions was not sufficient for testing the maxima in \(\sigma^{L_2,L_3}/\sigma^{L_1}\) curves.

Any significant drop of the \(\sigma^{L_3}/\sigma^{L_2}\) ratio, as observed by Datz et al.\(^{17}\) and Chang et al.\(^{18}\) for Au in the He\(^+\) data, at very low velocities was not observed by us. However, our experimental points do not clearly exhibit any tendency to follow the trend of the theoretical curves in this region.

It is worth mentioning that massive charged particles like H\(^+\) or He\(^+\) ions can be a sensitive probe in mapping the inner electronic wave functions. The bombarding ions employed in this work had E/A < 2.5 MeV/a.m.u. and so a much lower velocity than the L-subshell electrons. In this low velocity region the most probable collisions are those giving an ejected electron with almost zero kinetic energy and it is reasonable to approximate the final continuum electron wave function by a constant value equal to its value at the position of the nucleus for zero energy. The ionization cross section is then proportional to the square of the Fourier transform of the bound electron wave function and reflects the behavior of the momentum distribution of the inner shell electron states\(^{19}\).

Let \(\hbar q_o\) be the minimum momentum transfer from the incident ion to the bound electron. In a semiclassical picture\(^4\) the optimum penetration distance of the incident charged particle is \(b = q_o^{-1}\). When the impact parameter is of the order of \(b\) the ionization probability reaches a maximum. Since the energy transfer to the atom is most probably equal to the,
ionization energy $I$, we have finally $b = \frac{\hbar v}{I}$, where $v$ is the velocity of the ion.

For decreasing projectile velocities the main contribution to the cross section originates from smaller impact parameters and so the ionization cross sections at very low bombarding velocities give information on those portions of the electron wave functions nearest the nucleus, i.e., the cross section is sensitive to the high-momentum portions of the momentum distributions.

The ratios $\frac{\sigma^L_2}{\sigma^L_1}$ and $\frac{\sigma^L_3}{\sigma^L_1}$ displayed in Fig. 2 show that there is a dramatic change in the relative importance of the contribution from the various L-subshells to the total cross section. The contribution from the $L_1$-subshell is dominant at very low and very high projectile velocities, whereas the $2p$-subshells dominate in the intermediate region. These changes in the relative importance of the different subshells seem to reflect the electron density distribution in the L shell.

In Fig. 3 the Hf 2p and 2s H.F. radial functions $|R(nl; r)|^2$ calculated in Ref. 2 are shown. These functions are subjected to the normalization condition $\int_0^\infty |R(nl; r)|^2 r^2 dr = 1$. Below $r = 10^{-2}$ a.u. the inner 2s peak is largely dominant; it is responsible for the high momentum portion of the electronic momentum density. At very low energies this region gives the major contributions to the ionization cross sections. This feature is revealed by the dominance of $\frac{\sigma^L_1}{\sigma^L_1}$ at very low energies, the $\frac{\sigma^L_2}{\sigma^L_1}, \frac{\sigma^L_3}{\sigma^L_1}$ ratios dropping below 1 very rapidly as the energy of the incident ion decreases.
When the energies are such that the dominant impact parameter sweeps the region around the node of the 2s wave function, the $L_1$ ionization cross section ceases to increase and a plateau appears. The momentum amplitudes of the 2p state supplant the 2s ones and the ratios $\sigma^{L_1}_2, \sigma^{L_2}/\sigma^{L_1}_3$ become much greater than 1. A decrease in the ratios occurs when the outer 2s peak begins to play an important rôle. The plateau in the $\sigma^{L_1}/E$ curve is observed at a constant value of $\eta/\theta^2_{L_1}$. For the ten atoms examined in this work and in Ref. 1, it was found that the average value of $\eta/\theta^2_{L_1}$ is equal to 0.0131 with a dispersion of about 5%. In Fig. 4 the optimum penetration distance $b_{L_1}$ at the center of the plateau is plotted against the node of the 2s H.F. wave function. The vertical bars indicate the approximate indeterminacy in the position of the center of the plateau.

However, even for a rough estimate of $\eta/\theta^2_{L_1}$ at the plateau it is not essential to take for the final continuum electron wave function its value at the origin for zero energy. The kinetic energy of the electron can be made equal to zero after integrating over the position vector of the electron. The resulting form factor $|\mathcal{F}_{\text{HFS}}(Q)|^2$ (given in ref. 19, formula 46) shows a pronounced minimum at $Q = 1.385$ giving a constant value $\eta/\theta^2_{L_1} = 0.011$ at the plateau, in good agreement with the experimental results.

The H.F.S. wave functions are more realistic than the hydrogenic wave functions used in the framework of Born approximation. The 2s H.F.S. wave functions exhibit a node nearer the origin than the hydrogenic wave function. This
feature should provoke a further increase in the $L_I$ cross section at very low energies, as observed experimentally. So, it seems possible to test even fine details of the wave functions.

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REFERENCES


Table I - Adopted values of the fluorescence yields and Coster-Kronig factors.
FIGURE CAPTIONS

Fig. 1 - Scaled ionization cross section $\sigma^{L_1}_{I}/Z^2_1$ (in barns) versus E/A (in MeV/amu). The curves and the vertical scale labelled by a refer to Hf, by b to Ta, by c to W and by d to Ir.

Fig. 2 - Scaled ratios $\sigma^{L_1}_{I}/\sigma^{L_j}_{I}$ versus E/A. Notation is the same as in Fig. 1.

Fig. 3 - Hafnium H. F. radial functions $|R(n,l);r|^2$ calculated in Ref. 3.

Fig. 4 - The dominant impact parameter at the center of the plateau plotted against the non trivial zero of the 2s H. F. radial wave function.
<table>
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<th>Element</th>
<th>$\omega_1$</th>
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<th>$f_{13}$</th>
<th>$\omega_2$</th>
<th>$f_{23}$</th>
<th>$\omega_3$</th>
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<td>0.20</td>
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<td>0.30</td>
<td>0.16</td>
<td>0.28</td>
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</table>
Fig. 1
Fig. 2

E (MeV) / a.m.u.
Fig. 3
Fig. 4