

X-ray production induced by heavy ion impact: challenges and possible uses

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The emission of X-rays after the excitation with photons, electrons, or light ions (such as protons or deuterons), has been extensively studied. However, when heavier ions are used as primary radiation to induce this effect, other phenomena appear that are not present in the other cases. They include, for example, the formation of short-lived molecules, the capture of electrons from the target atom by the incoming ion, and a strong increase in the multiple ionization of the target atom. Usually, the ionization cross sections are higher as compared to those of photons, electrons, or protons. Furthermore, when thick targets are irradiated with heavy ions, there is a larger probability to create defects in the material, and also a higher stopping power in the target material. All these differences make the study of the X-ray production by heavy ions a problem not fully understood, and far from being applied in an extensive manner to the characterization of materials. In this work, an explanation of the basic phenomena is presented, together with possible uses of the emission of X-rays by the impact of the heavy ions, as an extension of the traditional method Particle Induced X-ray Emission (PIXE).

Keywords: X-rays; ionization; heavy ion impact; PIXE.

La emisión de rayos X debida a la excitación por fotones, electrones o iones ligeros (como protones o deuterones), se ha estudiado ampliamente. Sin embargo, cuando se usan iones más pesados como radiación primaria para inducir este efecto, aparecen otros fenómenos que no están presentes en los otros casos. Incluyen, por ejemplo, la formación de moléculas de vida corta, la captura de electrones del átomo blanco por parte del ion incidente, y un fuerte aumento en la ionización múltiple del átomo blanco. Usualmente, las secciones de ionización son mayores que en el caso de fotones, electrones o protones. Más aún, cuando se irradian blancos gruesos con iones pesados, hay una mayor probabilidad de crear defectos en el material, habiendo también un mayor poder de frenado en el material blanco. Todas estas diferencias hacen que el estudio de la producción de rayos X por el impacto de iones pesados sea un problema no entendido del todo. En este trabajo, se hace una explicación de los fenómenos básicos, junto con los posibles usos de la emisión de los rayos X por el impacto de iones pesados, como una extensión del método tradicional de Emisión de rayos X inducida por partículas (PIXE).

Descriptores: Rayos X; ionización; iones pesados; PIXE.

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1. Introduction

The phenomenon of characteristic X-ray emission, *i.e.*, ionization followed by the radiative de-excitation filling of an inner shell vacancy, induced by the impact of photons, electrons or heavier charged particles on atoms, has been known for several decades [1]. Specifically, the impact of ions heavier than protons and deuterons, which involves a number of processes that have not been fully described neither by theories or experiments due to their complexity [2], is still a problem subject to investigation, although not many research groups are involved in this task.

However, there is an increasing interest in the application of heavy ions for analysis with particle induced X-ray emission (PIXE), as they present higher X-ray yields, possibly improving PIXE sensitivity [3,4]. These papers proved that an exact knowledge of the ionization and further emission of X-rays due to heavy ion impact is necessary to obtain accurate results in quantitative analyses.

Therefore, the aim of this paper is to mention briefly the status of the research regarding the ionization and X-ray emission processes after heavy ion bombardment and to explain possible uses of these phenomena for PIXE analyses.

2. Basic physical processes in ionization and X-ray emission

The main physical process is the ionization of atomic inner shells by the impact of an energetic positive ion, followed by the de-excitation of the atom by the decay of an upper-shell electron to fill the vacancy, and the subsequent emission of an X-ray photon, to eliminate the excess energy in the atom (Fig. 1), including other processes, like the Auger electron emission or the radiative Auger process (simultaneous emission of a photon and an electron). Due to the existence of discrete energy levels in the atom, the electron expelled in the process described above may come from different atomic

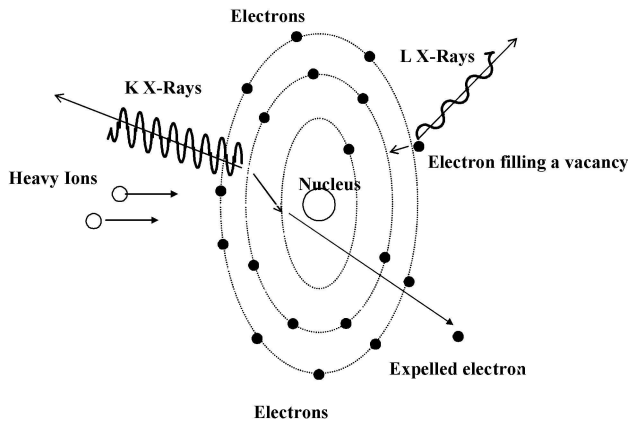


FIGURE 1. Schematics of the basic physical processes involved in X-ray emission by ion impact. The incoming ions expel electrons from inner shells, creating vacancies, which are subsequently filled by upper-shell electrons. Then, the excess energy is delivered by the ionized atom as X-rays, Auger electrons, or the combination of both (radiative Auger effect).

shells, as well as the electron filling the vacancy. The traditional nomenclature is known as the Siegbahn notation, while there is a more recent notation developed by the International Union of Pure and Applied Chemistry (IUPAC) [1]. Thus, a line created by a vacancy in the K-shell (principal quantum number $n = 1$) is called a K line, a vacancy in the L-shell (principal quantum number $n = 2$) gives rise to an L-line, and so on. Also, the electron filling the vacancy may have an origin from many other energy levels in the atom, limited only by the quantum selection rules for electronic transitions. This fact makes possible to have a number of K, L, M or other lines, which must also be identified. Therefore, the most intense line in the K group is called K_{α} , and the next one is the K_{β} . Each one of these lines may also be composed of a certain number of lines, which are recognized by the subscripts 1, 2, 3, etc., so there are $K_{\alpha 1}$, $K_{\alpha 2}$, $K_{\beta 1}$, $K_{\beta 2}$... lines.

The probability of producing the X-ray photons of a particular line, or X-ray production cross section, is a physical magnitude that depends on several factors, such as the projectile, its energy, and the target atom. For the K lines, it is related to the probability of ionizing the atom, or ionization cross section, by the equation

$$\sigma_{X,i} = \sigma_{I,K} \omega_K P_i, \quad (1)$$

where $\sigma_{X,i}$ is the X-ray production cross section, $\sigma_{I,K}$ is the K-shell ionization cross section, ω_K is the fluorescence yield, and P_i is the relative intensity of all the possible transitions included in the line i . The fluorescence yield is the ratio of the number of emitted X-ray photons to the number of total produced vacancies in the K shell. For the L shell (and upper shells), the expressions are more cumbersome because it is possible to have non-radiative transitions from different subshells within the shells L_1 , L_2 , and L_3 . If a vacancy is created in the L_1 subshell, it may be filled by an electron from the L_2 subshell, which in turn may be filled by an electron coming from the L_3 subshell. The net result is a vacancy in L_3 . These

processes are known as *Coster-Kronig transitions*. It is possible to obtain for the L X-ray production cross sections of the most common lines the following equations:

$$\sigma_{X,L\ell} = (\sigma_{L_1} f_{13} + \sigma_{L_1} f_{12} f_{23} + \sigma_{L_2} f_{23} + \sigma_{L_3}) \omega_3 F_{3\ell}; \quad (2)$$

$$\sigma_{X,L\beta} = \sigma_{L_1} \omega_1 F_{1\beta} + (\sigma_{L_1} f_{12} + \sigma_{L_2}) \omega_2 F_{2\beta} + (\sigma_{L_1} f_{13} + \sigma_{L_1} f_{12} f_{23} + \sigma_{L_2} f_{23} + \sigma_{L_3}) \omega_3 F_{3\beta}; \quad (3)$$

$$\sigma_{X,L\gamma} = \sigma_{L_1} \omega_1 F_{1\gamma} + (\sigma_{L_1} f_{12} + \sigma_{L_2}) \omega_2 F_{2\gamma}; \quad (4)$$

$$\sigma_{X,L\ell} = (\sigma_{L_1} f_{13} + \sigma_{L_1} f_{12} f_{23} + \sigma_{L_2} f_{23} + \sigma_{L_3}) \omega_3 F_{3\ell}. \quad (5)$$

Here, the σ_{L_i} are the ionization cross sections of an individual L_i subshell, ω_i is the fluorescence yield of the i subshell, f_{ij} is the probability for a Coster-Kronig transition between subshells i and j , while F_{nx} is the probability of producing a radiative transition, taken as the fraction of X-ray photons originated from a vacancy in the L_n subshell, contributing to the L_x line.

3. Direct ionization and X-ray emission

Two aspects must be studied in this subject: theory and experimental results. Complete listings of papers dealing with the measurement of ionization by K and L-shell ionization by heavy ion impact are given by De Lucio and Miranda [5] and Lugo-Licona [6]. The ECPSSR theory of Brandt and Lapicki [7] is the most successful model in describing the ionization by ion impact [8,9]. This theory is a modification of the Plane Wave Born Approximation (PWBA). It considers effects such as the ion energy loss after the collision (E), the Coulomb deflection in the ion trajectory (C), the modification of the atomic electron energy states through a perturbed stationary states model (PSS), and an adjustment in the mass of the electron, due to relativistic effects (R). There are other improvements to this model. For example, the United Atom (UA) correction to the ECPSSR model (or ECPSSR-UA) includes a modification in the binding energies of the target electrons due to the presence of the projectile [10]. Furthermore, Benka *et al.* [11] introduced a modification to the ECPSSR model in order to take into account the formation of molecular orbitals (MO) during the ion-atom collision, following a UA approach. They change the ECPSSR model, (target atom effective charge, reduced binding energy and binding-polarization variable). This new model was known as MECPSSR. Here, there are two adjustable parameters, present in a seemingly *ad hoc* function used to establish a transition from the separated atom and the ECPSSR-UA for heavy ions. They calculated these constants to optimize the agreement between their data for K X-rays from several elements (like Ti, Fe, and Cu) after impact with ^{16}O ions and their proposed model. There is still a question whether the parameters are valid also for other ions, different incident energy ranges, or target atomic numbers. The last question is also related to the symmetry in the collisions, that is, how similar the atomic numbers of the ion and the target

atoms are. A further improvement is the consideration of intrashell (IS) transitions for L-shell ionization. Sarkadi and Mukoyama developed means of accounting for these phenomena [12-14].

In contrast, Montenegro and Sigaud [15] elaborated analytical expressions for evaluating the ionization cross sections through adiabatic perturbations, only applicable to the K-shell, known as a direct MO model. In the adiabatic limit, the ionization is predominant at internuclear distances smaller than the K-shell radius. Here, the Coulomb excitation of an electron occupying a MO can be seen as a superposition of two components, each one corresponding to the two involved nuclei.

In a different aspect, it is important to discuss the two groups of atomic parameters: fluorescence yields and Coster-Kronig factors, and emission rates. In the first case, traditionally, the semiempirical tables published by Krause in 1978 have been used [16]; however, there exist also the relativistic Dirac-Hartree-Slater calculations of Chen *et al.* [17]. Puri *et al.* [18] published a more recent interpolation of the latter values for the L-shell. Regarding the emission rates, it can be mentioned that three approaches for their calculations have been followed: the semiempirical tables by Salem *et al.* [19], the relativistic Dirac-Hartree-Slater calculations by Scofield [20], and the Dirac-Fock predictions by Scofield [21], interpolated later by Campbell and Wang [22]. There is a more recent compilation given by Campbell for the L-shell atomic parameters [23], although in a limited atomic number range. Miranda *et al.* [24] demonstrated that the use of different databases for atomic parameters, namely emission rates, fluorescence yields and Coster-Kronig transitions, has a significant effect on the theoretical predictions for the L-shell X-ray emission.

4. Multiple ionization

The ejection of more than one electron from the target atom, known as multiple ionization (MI), alters one of the most important parameters involved in X-ray production, *i.e.*, the fluorescence yield. A simple heuristic model was given by Lapicki *et al.* [25], which is used to correct fluorescence yield values. This adjustment takes as a basic assumption that the fluorescence yields change through the creation of holes in the outer shells by the incident ions, with an equal probability for each shell, calculated through the Binary Encounter Approximation, or BEA [26]. This avoids the difficult calculation of outer shell ionization probabilities by other, more refined, theories. There is a recent application to the ionization of heavy elements (Re, Pt, and Au) by $^{12}\text{C}^{3+}$ ions [27], while Lugo-Licona and Miranda used it to compare with cross-section measurements in rare earth elements bombarded by ^{10}B [28], and ^{12}C and ^{16}O ions [29]. Other authors [30-32] have considered this effect when heavy projectile ions are used, such as He or C. Also, the M-shell was studied by Yu *et al.* [33], and by Braich *et al.* [34]. Generally, better agreement between theory and experiment is found with this correction.

There is also an alternative method proposed by Tanis *et al.* [35] for the fluorescence yield correction, based on peak energy shifts and intensity ratios. It is possible to correlate those energy shifts with the number of 2p vacancies; taking these values and the respective measured intensity ratios $I[\text{K}_\beta]/I[\text{K}_\alpha]$, the number of 3p vacancies are then determined. Thus, the number of 2p and 3p vacancies provides the change in the fluorescence yield with projectile energy.

There is still a question about the role of multiple ionization effects on X-ray emission. There are contradictory and uncertain arguments trying to explain why the X-ray emission should increase or diminish [27].

5. Electron capture

An additional effect is the capture of electrons from the target inner shells by the incoming ions, which contributes in a non-negligible manner to K-shell ionization, especially for symmetric collisions. To provide a more accurate description of the measured X-ray production cross sections, it is necessary to include this phenomenon in the theoretical calculations. Electron capture (EC) cross sections are usually calculated with the Oppenheimer-Brinkman-Kramer formulas of Nikolaev [36]. According to the standard ECPSSR theory [7,37] the contribution of EC to ionization increases with increasing projectile energy. As a rule, it is necessary to include this effect in order to improve the agreement among theoretical predictions and experimental results.

6. Anisotropy in L and upper shells X-ray emission

A further event that may occur during the production of L- or M-shell X-rays is the anisotropy in the emission of the photons. The particular atom can be aligned in the direction of the incoming projectile, thus setting a preferential symmetry. This alignment is the result of the different ionization cross section values for changing projections of the angular momentum along the beam direction. To study this effect, it is possible to measure angular distribution of the emitted X-rays or the polarization of those photons [38]. Although several studies have been published to explain this effect, it is not possible hitherto to provide a complete explanation [39]. It must be mentioned that although there is an extensive work in the measurement of L X-ray production cross sections, the anisotropy has seldom been taken into account. Furthermore, quantitative analyses using PIXE, X-ray fluorescence (XRF) or electron probe microanalysis (EPMA) usually do not consider this process. As expected, it may induce some inaccuracies in the results, although they have not been estimated to date.

7. Applications

The applications of PIXE have been extensively described by Johansson and Campbell [40]. However, the use of heavy ions has been rather limited so far. Examples are given by Ozafrán [3,4] and Amartaivan *et al.* [41], employing heavy

ions at high incident energies for elemental analysis. Their conclusion is that this combination provides better sensitivity than the usual arrangement of protons with 2-3 MeV energies. Ecker and coworkers used [42] 14 MeV Ni ions to determine Fe traces in glass. Although it has not been used hitherto, it is also suggested that the differences in ionization and stopping cross sections within a target material when different ions are used may be applied in elemental depth profiling. A better depth resolution should be expected when heavy ions are chosen as projectiles. Nevertheless, accurate measurements and simple theoretical predictions of stopping cross sections in compounds are still needed. It must be emphasized, also, that these ions may produce significantly more defects in the target than protons, deuterons or helium ions, damaging the sample to be studied.

8. Conclusions

The description of the ionization and further X-ray production in atoms bombarded with heavy ions remains as an open problem. Although improvements have been made, it still requires both theoretical and experimental work. Furthermore, the applications of heavy ions are not fully developed to date, possibly due to the inaccuracies found in the understanding of the basic processes and the possible damage to samples.

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1. R.E. Van Grieken and A.A. Markowicz, eds. *Handbook of X-ray Spectrometry*, 2nd ed. (John Wiley, New York, 2002).
2. W. Wölfl, Heavy Ion Physics. In: V. Ceausescu and I.A. Dorobantu, (Eds.) Predeal International Summer School (Central Institute of Physics, Bucharest, 1976) p. 43.
3. M.J. Ozafrán *et al.*, *Nucl. Instr. and Meth. B* **74** (1993) 542.
4. M.J. Ozafrán *et al.*, *Nucl. Instr. and Meth. B* **99** (1995) 384.
5. O.G. de Lucio and J. Miranda, *Rad. Phys. Chem.* **73** (2005) 189.
6. M.F. Lugo-Licona, *Secciones eficaces de producción de rayos X L por impacto de iones pesados en tierras raras*, Ph.D. thesis (Universidad Autónoma del Estado de México, Toluca, Mexico, 2004).
7. W. Brandt and G. Lapicki, *Phys. Rev. A* **23** (1981) 1717.
8. G. Lapicki, *Nucl. Instrum. Meth. Phys. Res. B* **189** (2002) 8.
9. G. Lapicki, *X-ray Spectrom.* **34** (2005) 269.
10. L. Sarkadi and T. Mukoyama, *Nucl. Instr. and Meth. B* **61** (1991) 167.
11. O. Benka, M. Geretschlager, and H. Paul, *J. Phys. Coll. C9*, suppl. 12, **48** (1987) 251.
12. L. Sarkadi and T. Mukoyama, *J. Phys. B* **14** (1980) L225.
13. L. Sarkadi and T. Mukoyama, *Nucl. Instrum. Meth. B* **4** (1984) 286; L. Sarkadi, *J. Phys. B* **19** (1986) 2319.
14. L. Sarkadi, *J. Phys. B* **19** (1986) L755; L. Sarkadi and T. Mukoyama, *ibid.* **20** (1987) L559; *J. Phys. B* **23** (1990) 3849.
15. E.C. Montenegro and G.M. Sigaud, *J. Phys. B* **18** (1985) 299.
16. M.O. Krause, *J. Phys. And Chem. Ref. Data* **8** (1979) 307.
17. S. Puri, D. Mehta, B. Chand, N. Singh, and P.N. Trehan, *X-ray Spectrom.* **22** (1993) 358.
18. M.H. Chen, B. Crasemann, and H. Mark, *Phys. Rev. A* **24** (1981) 177.
19. S.I. Salem, S.L. Panossian, and R.A. Krause, *At. Data and Nucl. Data Tables* **14** (1974) 91.
20. J.H. Scofield, *At. Data and Nucl. Data Tables* **14** (1974) 121.
21. J.H. Scofield, *Phys. Rev. A* **10** (1974) 1507.
22. J.L. Campbell and J.X. Wang, *At. Data and Nucl. Data Tables* **43** (1989) 281.
23. J.L. Campbell, *At. Data Nucl. Data Tables* **85** (2003) 291.
24. J. Miranda, C.M. Romo-Kröger and M. Lugo-Licona, *Nucl. Instr. and Meth. B* **189** (2002) 21.
25. G. Lapicki *et al.*, *Phys. Rev. A* **34** (1986) 3813.
26. D.H. Madison and E. Merzbacher, Theory of Charged-Particle Excitation. In *Atomic Inner-Shell Processes*, B. Crasemann, ed. (Academic Press, New York, 1975) Vol. I, 1.
27. G. Lapicki *et al.*, *Phys. Rev. A* **70** (2004) 062718.
28. M. Lugo-Licona and J. Miranda, *Nucl. Instrum. Meth. B* **219-220** (2004) 289.
29. M. Lugo-Licona, J. Miranda, and C.M. Romo-Kröger, *J. Radioanal. Nucl. Chem.* **262** (2004) 391.
30. R. Mehta *et al.*, *J. Phys. B* **28** (1995) 1187.
31. J. Semaniak *et al.*, *Phys. Rev. A* **52** (1995) 1125.
32. Y.C. Yu *et al.*, *J. Phys. B* **30** (1997) 5791.
33. Y.C. Yu *et al.*, *Phys. Rev. A* **52** (1995) 3836.
34. J.S. Braich, P. Verma, and H.R. Verma, *J. Phys. B* **30** (1997) 2359.
35. J.A. Tanis, S.M. Shafroth, W.W. Jacobs, T. McAbee, and G. Lapicki, *Phys. Rev. A* **31** (1985) 750.
36. V.S. Nikolaev, *Zh. Eksp. Teor. Fiz.* **51** (1966) 1263; [*Sov. Phys. JETP* **24** (1967) 847].
37. G. Lapicki and F.D. McDaniel, *Phys. Rev. A* **22** (1980) 1896.
38. O.G. de Lucio and J. Miranda, *Rev. Mex. Fís.* **50** (2004) 319.
39. O.G. de Lucio and J. Miranda, *Nucl. Instr. and Meth. B* **248** (2006) 47.
40. S.A.E. Johansson and J.L. Campbell, *PIXE: A Novel Technique for Materials Analysis* (John Wiley, Chichester, 1988).
41. Ts. Amartaivan, K. Ishii, H. Yamazaki, S. Matsuyama, A. Suzuki, T. Yamaguchi, S. Abe, K. Inomata, and Y. Watanabe, Proc. 10th International Conference on Particle Induced X-ray Emission and its Analytical Applications (Portoroz, Slovenia, 2004), p. 823-1.
42. K.H. Ecker, H.P. Weise, and K.L. Merkle, *Mikrochim. Acta* **133** (2000) 313.