

NIST NSRDS 164

**NIST Database of Cross Sections for
Inner-Shell Ionization by Electron
or Positron Impact**

**Version 1.0
User's Guide**

Xavier Llovet
Francesc Salvat
David Bote
Francesc Salvat-Pujol
Aleksander Jablonski
Cedric J. Powell

<http://dx.doi.org/10.6028/NIST.NSRDS.164>

NIST NSRDS 164

NIST Database of Cross Sections for Inner-Shell Ionization by Electron or Positron Impact

Version 1.0
User's Guide

Xavier Llovet
Centres Científics i Tecnològics, Universitat de Barcelona
Barcelona, Spain

Francesc Salvat
David Bote
Facultat de Física, Universitat de Barcelona
Barcelona, Spain

Francesc Salvat-Pujol
Institut für Theoretische Physik, Johann Wolfgang Goethe Universität
Frankfurt am Main, Germany

Aleksander Jablonski
Institute of Physical Chemistry, Polish Academy of Sciences
Warsaw, Poland

Cedric J. Powell
Materials Measurement Science Division
Materials Measurement Laboratory

This publication is available free of charge from:
<http://dx.doi.org/10.6028/NIST.NSRDS.164>

August 2014



U.S. Department of Commerce
Penny Pritzker, Secretary

National Institute of Standards and Technology
Patrick D. Gallagher, Under Secretary of Commerce for Standards and Technology and Director

The National Institute of Standards and Technology (NIST) uses its best efforts to deliver a high quality copy of the database and to verify that the data contained therein have been selected on the basis of sound scientific judgment. However, NIST makes no warranties to that effect, and NIST shall not be liable for any damage that may result from errors or omissions in the database.

For a literature citation, the database should be viewed as a book published by NIST. The citation would therefore be:

X. Llovet, F. Salvat, D. Bote, F. Salvat-Pujol, A. Jablonski and C.J. Powell, *NIST Database of Cross Sections for Inner-Shell Ionization by Electron or Positron Impact*, Version 1.0, National Institute of Standards and Technology, Gaithersburg, Maryland (2014).

©2014 by the U.S. Secretary of Commerce on behalf of the United States of America. All rights reserved. No part of this database may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior written permission of the distributor.

Certain trade names and other commercial designations are used in this work for the purpose of clarity. In no case does such identification imply endorsement by the National Institute of Standards and Technology nor does it imply that the products or services so identified are necessarily the best available for the purpose.

Microsoft, Windows® 95, Windows® 98, Windows® 2000, Windows® NT, Windows® XP, Windows® Vista, Windows® 7, and Windows® 8 are registered trademarks of the Microsoft Corporation.

TABLE OF CONTENTS

| | |
|---|----|
| 1. Introduction | 1 |
| 2. Getting started | 1 |
| 2.1 Database content | 1 |
| 2.2 System requirements | 1 |
| 2.3 Installation of the database and GUI | 1 |
| 3. Quantities available from the database | 2 |
| 4. Structure and operation of the GUI | 3 |
| 4.1 Visualizing the cross sections | 6 |
| 4.2 Exporting data | 9 |
| 5. References | 10 |
| Appendix A. Uncertainties of cross sections from the database | 12 |
| Appendix B. Selection of inner-shell binding energies | 15 |
| Appendix C. Contacts | 17 |

1. INTRODUCTION

Cross sections for the removal of atomic inner-shell electrons by electron impact are needed in many branches of physics including atomic physics, plasma physics, radiation physics, materials analysis by electron-probe microanalysis (EPMA), surface analysis by Auger-electron spectroscopy (AES), and thin-film analysis by electron energy-loss spectroscopy (EELS). For example, these cross sections are utilized in Monte Carlo simulations of EPMA and AES measurements, particularly to derive correction factors to account for diminished or enhanced EPMA and AES signal intensities from heterogeneous specimens.

The present database contains tables of cross sections for ionization of inner shells (K shells, and L and M subshells) of atoms by impact of electrons and positrons. These tables were calculated using the theory and numerical algorithms described by Bote and Salvat [1].

A Java graphical user interface (GUI) is provided to visualize the contents of the database files, to evaluate and visualize derived quantities (vacancy-production cross sections, Auger and x-ray emission cross sections), and to export cross-section tables as formatted ASCII files.

2. GETTING STARTED

2.1 Database content

- Graphical user interface, file **NIST164.jar**
- Windows installer, file **WIN_NIST164.zip**
- This user's guide, file **NIST SRD164 User Guide.pdf**

These files can be downloaded from a NIST web site: <http://www.nist.gov/srd/surface.cfm>. As explained below, the Java file (**NIST164.jar**) can be run on any computer with the Java Runtime Environment (JRE) installed while the second file (**WIN_NIST164.ZIP**) contains a compressed installer so that Windows users can, if they wish, install the database on their computers; these installations also require the JRE. Arrangements can also be made for the database files and the user's guide to be distributed on a CD-ROM.

2.2 System requirements

1. Any computer with the JRE installed. This software is available for free download at <http://www.java.com>. Detailed supporting information is available on this site.
2. A monitor with resolution higher than 1024 by 768 pixels.

2.3 Installation of the database and GUI

(a) Java file

The database and the GUI are contained in a single, stand-alone file named **NIST164.jar**. This software does not require installation; simply have that file accessible in your computer (either on the hard disk or in another memory storage device). The GUI is started by entering

the command **java -jar NIST164.jar** from the directory where the file **NIST164.jar** is located. This command may also open a Java console window. If the executable **javaw** is available on your computer, the alternative command **javaw -jar NIST164.jar** starts the GUI without opening the console window.

The java commands in the previous paragraph assume that the paths of the executables **java** and **javaw** are defined in the **PATH** environment variable; otherwise, we would have to specify the path of the Java executable (*e.g.*, **C:\Program Files (x86)\Java\jre7\bin\javaw -jar NIST164 .jar** in Windows 7, default path). In some platforms, the Java installation software automatically includes the paths of the Java executables in **PATH**; otherwise, the user should do it manually, as described in <http://docs.oracle.com/javase/tutorial/essential/environment/paths.html>.

If the extension “**.jar**” is associated to Java¹, you can alternatively start the GUI directly by double clicking the mouse on the **NIST164** icon. To remove the GUI from your computer, simply delete the file **NIST164.jar**.

(b) Installation on a Windows computer

To install the software from the **WIN_NIST164.zip** file, proceed as follows:

- Unzip the file **WIN_NIST164.zip** into a directory on the user’s personal computer,
- Double-click the **Setup.exe** icon (showing the computer),
- Follow instructions on the screen.

By default, the database is installed in the directory **C:\PROGRAM FILES\NIST\ NIST164**. Furthermore, the icon **NIST164** is added to the list of programs that appears after clicking the **Start** button and choosing **All Programs**. After installation, you can create a shortcut to the **NIST164** program (by dragging the **NIST164** program icon with the mouse from the program list to the desktop). To remove the database, follow the conventional uninstall procedure.

(c) Other information

The program output uses US locale settings to ensure that quantities in output files are written in the common numerical style, **+d.dddddE+dd**, irrespective of the computer’s configuration. However, you should be aware that some numerical quantities shown in the GUI are written in local style (the figures below were produced with Spanish locales).

3. QUANTITIES AVAILABLE FROM THE DATABASE

The database consists of 198 ASCII files containing tables of cross sections for ionization of the K shell, and L and M subshells² of neutral atoms of the elements, from hydrogen to

¹ In Windows, to associate **jar** files with Java, open **Windows Explorer**, find the **NIST164.jar** file, right click on its icon and, in the emerging context menu, select the **Open with** option and choose Java as the default program. Alternatively, click the **Start** button, and then click **Default Programs**, and set Java as the default program for the **jar** files.

² For simplicity, in the following text and in the GUI we use the term “shell” to refer both to shells (sets of one-electron orbitals with the same principal quantum number) and subshells (sets of orbitals with the same values of the principal, orbital angular momentum, and total angular momentum quantum numbers).

einsteinium, by electron and positron impact. The tables cover a range of kinetic energies E that extend from the ionization threshold (the binding energy of the active shell) up to 1 GeV. These tables were calculated from a combination of the relativistic distorted-wave and the plane-wave Born approximations, as formulated in Ref. [1], using computer programs written by Bote and Salvat. References [2,3] describe simple parameterizations of the present shell cross sections as functions of E , accurate to about 1 %, which can be used for rapid evaluation within a computer program. Exhaustive comparisons of the calculated cross sections for inner-shell ionization by electron impact with available experimental data are presented in Ref. [4] where it was found that the overall root-mean-square deviation between measured and calculated cross sections was 10.9 %. Further information on estimates of uncertainties of cross sections from the database is given in Appendix A. No evaluations have yet been made of the calculated cross sections for inner-shell ionization by positrons because of the paucity of experimental data. Nevertheless, it is believed that the algorithms for the latter calculations [1] have been validated by the comparisons between calculated and measured cross sections for inner-shell ionization by electron impact.

For the sake of theoretical consistency, the shell binding energies employed in Refs. [1,2] were the negative of the Dirac-Hartree-Fock-Slater (DHFS) energy eigenvalues [5], which are close, but not equal, to the experimental binding energies (see the Appendix in Ref. [4]). The latter are better approximated by the values compiled by Carlson [6] and by Williams [7]. To correct for the differences between the DHFS eigenvalues and experimental ionization energies [6,7], we add a constant value to the kinetic energy of the projectile which shifts the ionization threshold to its experimental value [3]. The GUI allows the user to select a particular source of binding energies (DHFS, Carlson, or Williams) or even to define alternative binding energies for each shell. Note that all energies are expressed in electron-volts (eV), both in the database and in the GUI. Further information on selection of binding energies is given in Appendix B.

The GUI also provides cross sections for the production of a vacancy in each shell, and for the emission of Auger electrons and characteristic x rays resulting from a single vacancy in a given shell. Radiative and non-radiative transitions are denoted using the respective notations, S0-S1 and S0-S1-S2, where SI indicates the shells involved in the transition. These emission cross sections are calculated directly from the ionization cross sections in the database, using transition probabilities from the Evaluated Atomic Data Library (EADL) of Perkins *et al* [8], as described in Ref. [4]. The energies of x rays emitted in radiative transitions resulting from single vacancies in the K and L shells are from Deslattes *et al.* [9]. X-ray energies for transitions of vacancies in M shells are from Bearden's reevaluation of experimental x-ray wavelengths [10], or from the EADL when the transition is not included in Bearden's tables. The energies of Auger electrons are taken from the EADL, and correspond to non-radiative transitions of a single vacancy in the active shell.

4. STRUCTURE AND OPERATION OF THE GUI

The GUI presents a single window (Fig. 1) with a menu bar, a set of combo boxes, element-selection buttons, a plot area, and a cross-section list. The displayed information is determined by the states of the combo boxes. The format of the plot can be modified by accessing a context menu, which is activated by pressing the right button of the mouse when the pointer is within the plot area.

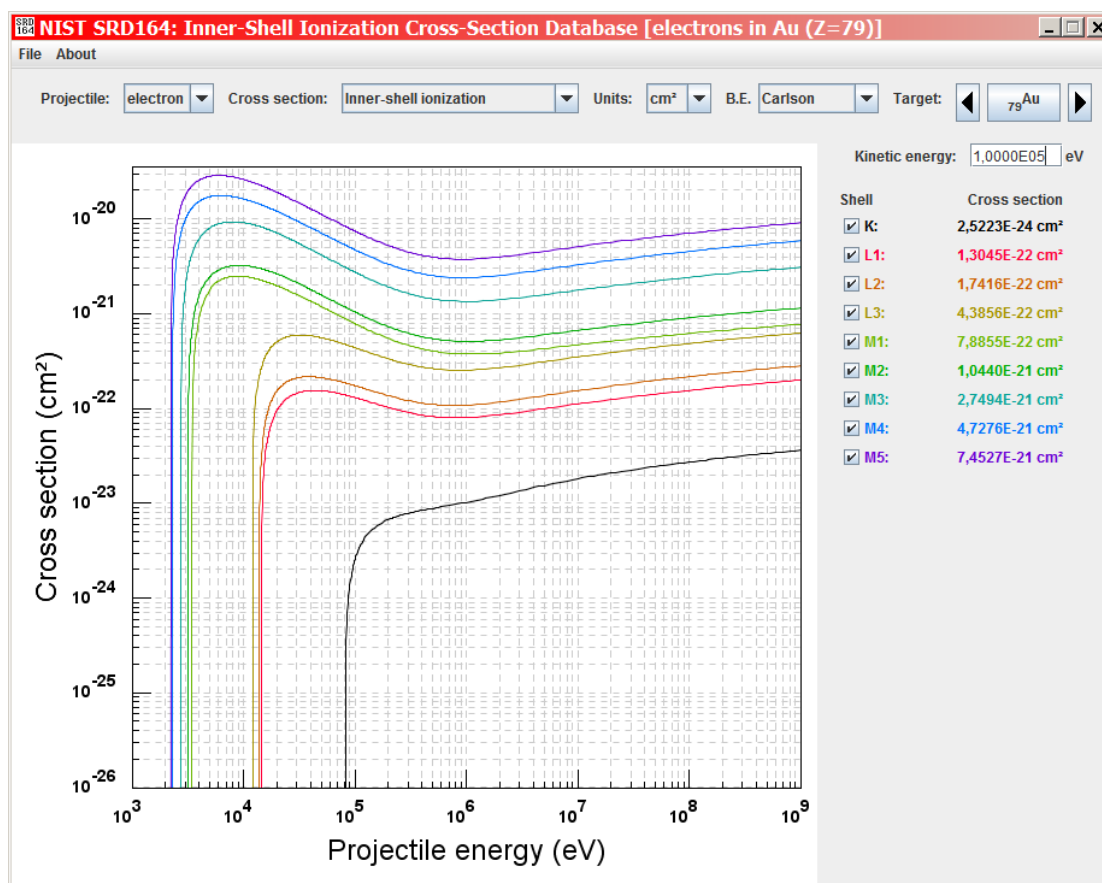


Figure 1. Opening GUI window.

Combo boxes and buttons:

- **Projectile:** electron or positron.
- **Cross section:** cross sections can be plotted, and delivered, for the processes of impact ionization of inner shells, vacancy production, Auger-electron emission, and x-ray emission.
- **Units:** cm², Angstrom (Å² = 10⁻¹⁶ cm²), or barn (= 10⁻²⁴ cm²).
- **Binding energies:** can be selected among the following alternatives: Dirac-Hartree-Fock-Slater (**DHFS**) energy eigenvalues, values compiled by **Carlson** [6], values recommended by **Williams** [7], or values entered by the user. Figure 2 shows the window which is opened if the latter option is chosen. The default binding energies are those of Carlson. See Appendix B for further information.
- **Target:** A neutral atom with atomic number from 1 to 99. The arrow buttons move to the previous or to the following element in the periodic table. Clicking on the **target** box opens a window with the periodic table (Fig. 3), where a desired element can be selected by clicking on its symbol.

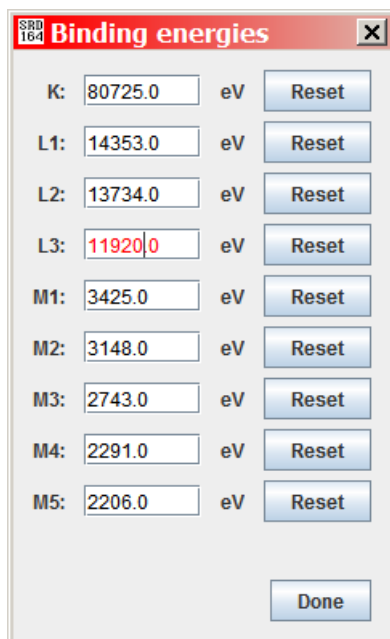


Figure 2. Window that is opened if the **user defined** option is chosen to modify the binding energies for a shell of the selected atom. In this example, the binding energies for Au of **Williams** [7] are shown with the exception of the Au L₃-subshell binding energy which has been changed from 11 919 eV to 11 920 eV. The **reset** buttons enable resets to the previously selected binding energies (*i.e.*, DHFS, Carlson, or Williams).

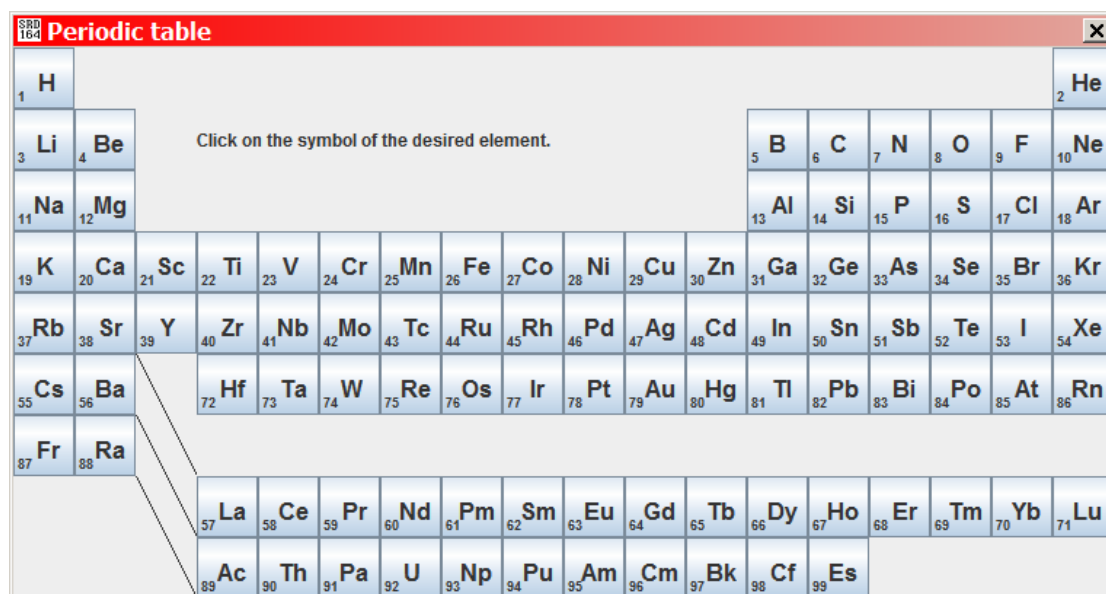


Figure 3. Periodic table.

Menu bar items:

- **File:** allows the user to **export data** to an ASCII file, and to **exit** the GUI.
- **About:** displays the NIST **disclaimer**, and a window with information **about** the version, year, and authors of the database and the GUI.

4.1 Visualizing the cross sections

When the GUI is started, its window opens in a pre-defined state (ionization cross sections of Au by electron impact as a function of projectile energy, as in Fig. 1). The user can modify the selections in the combo boxes to display the desired cross sections for the selected target atom and projectile. Both the plotted curves and the cross-section list will change each time a combo-box selection is modified. Note that the color of the displayed curves indicate the corresponding shell, as shown in the cross-section list at the right of the GUI window.

Binding energies can be selected among the three options provided in a drop-down list (DHFS, Carlson, and Williams) or entered by the user by modifying the corresponding values in a window (Fig. 2) with a list of shells and binding energies from the previously selected source.

The mouse actions are only active when the pointer is inside the plot area. Pressing the left button, we can drag the mouse to select a portion of the plot and zoom in. The right button of the mouse opens a context menu (Fig. 4), which allows changing to previous or later zoom levels, modifying the intervals on the axes, selecting a linear or logarithmic scale for each axis, displaying/hiding a grid over the plot area, and displaying/hiding vertical and horizontal lines from the cursor position. The values in the cross-section list at the right side of the GUI window correspond to the energy defined by the (horizontal) position of the cursor. Indeed, these values change when the pointer moves within the plot area. Alternatively, numerical values of cross sections at a given energy can be visualized by entering that energy in the provided text field at the top of the list. Appendix A gives information on uncertainties of the cross sections.

Cross sections for the emission of Auger electrons and x rays can be displayed for a single shell at a time, either for single transitions or for a group of transitions selected by the user from a list in a separate window showing the allowed transitions with their energies (Fig. 5). Note that transitions in the windows shown in Fig. 5 can be sorted according to energy or shell, either in ascending or descending order, by clicking on the table headings.

The user can select the desired transitions from the windows shown in Fig. 5. After clicking the **apply** button, the GUI (Fig. 6) will display the cross sections for the selected transitions as well as their sum (**total**). When more than eight transitions are selected, only the eight having the largest cross sections are displayed in the plot; however, the output file contains cross-section tables for all of the selected transitions. Figure 6 is an example of a display of the cross sections for x-ray emission as a function of projectile energy for each of the four Au x-ray transitions selected in Fig. 5. Display of the total cross section is useful, *e.g.*, in energy-dispersive EPMA, for describing the relative intensities of unresolved characteristic lines.

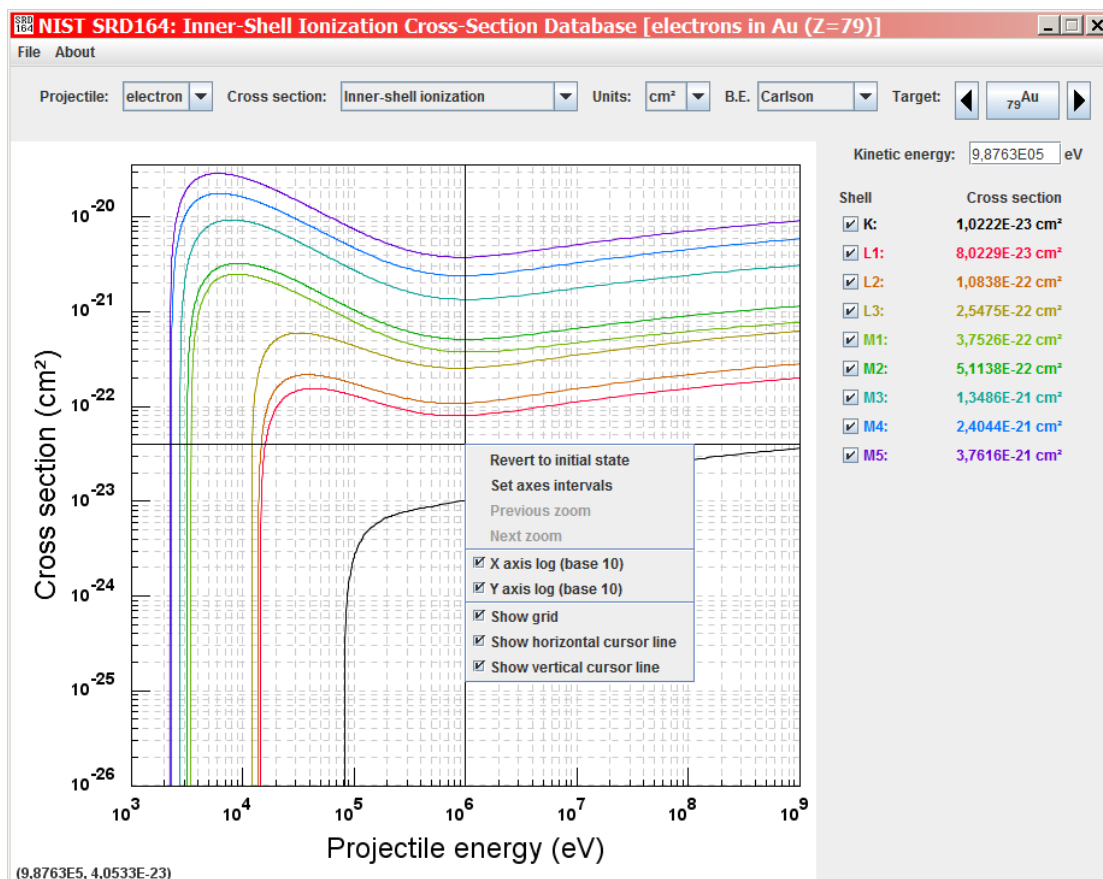


Figure 4. Context menu activated from the plot area with the right button of the mouse.

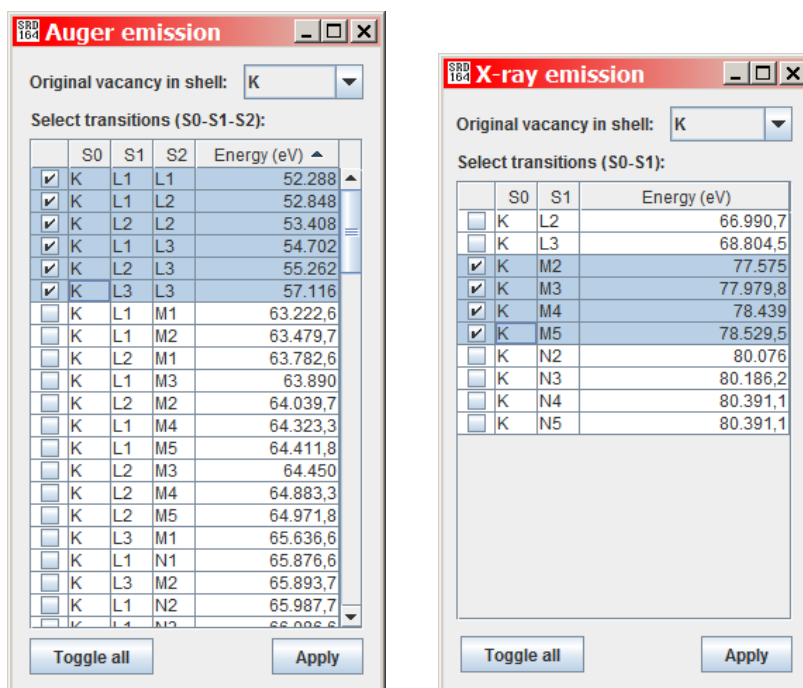


Figure 5. Windows with transitions and transition energies for **Auger-electron emission** (left) and **x-ray emission** (right) from Au.

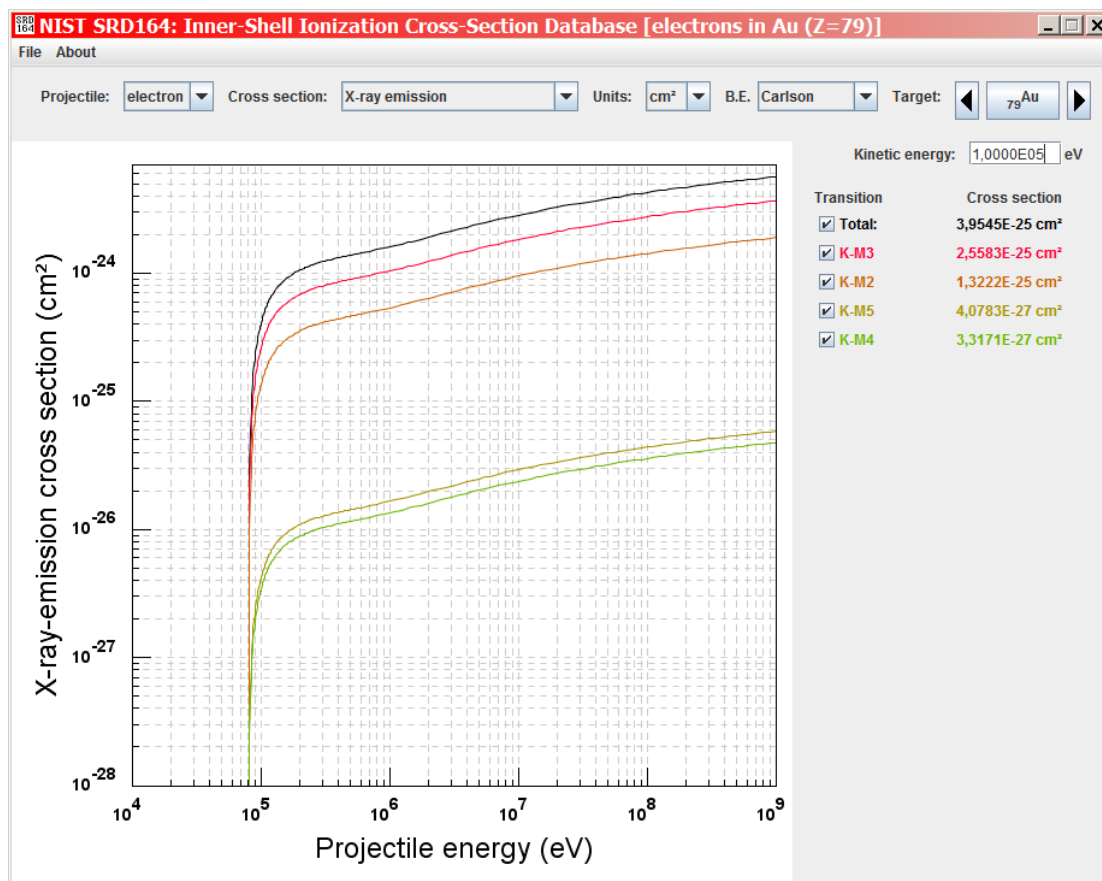


Figure 6. Total x-ray emission cross section (black curve) and individual x-ray emission cross sections (lower curves) for the four Au x-ray transitions selected in Fig. 5.

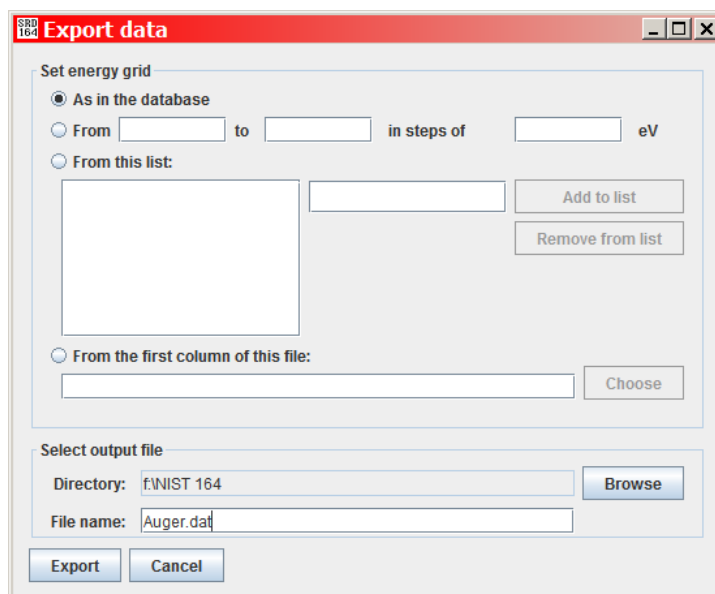


Figure 7. Options in the export window (**export data** in the **file** menu).

4.2 Exporting data

The cross sections displayed in the plot area can be exported as a table to an ASCII file, formatted as multiple columns separated by blanks. The first column gives the energies (in eV), and the following columns contain the cross sections for each shell that appeared in the plot.

The generation of the output file is initiated by selecting **export data** in the **file** menu which opens a window (Fig. 7) where the user can define the grid of energies (as in the database, uniform, defined by a list of values, or read from the first column of an existing file), and the path and name of the output file. By default, the **export data** window opens in the directory where the **NIST164.jar** file is located. The **directory** button can be used to choose an alternative directory for the output file. Finally, the user enters a suitable name for the output file (and an extension, if desired) in the **file name** box.

The output file contains a comment header with the information necessary to identify the cross sections contained in the file, the adopted area unit, and the binding energies employed. In the case of cross sections for emission of Auger electrons or x rays, the active shell, the considered transitions (as selected in the window of Fig. 5), and their energies are also listed.

The internal database files are not visible to the user. They can be obtained, if desired, first by plotting ionization cross sections on the GUI and then by exporting the data using the energy grid option **as in the database** (as shown in Fig. 7).

5. REFERENCES

- [1] D. Bote and F. Salvat, “Calculations of inner-shell ionization by electron impact with the distorted-wave and plane-wave Born approximations,” *Phys. Rev. A* **77**, 042701 (2008).
- [2] D. Bote, F. Salvat, A. Jablonski, and C. J. Powell, “Cross sections for ionization of K, L, and M shells of atoms by impact of electrons and positrons with energies up to 1 GeV: Analytical formulas,” *At. Data and Nucl. Data Tables* **96**, 871 (2009).
- [3] D. Bote, F. Salvat, A. Jablonski, and C. J. Powell, “Erratum. Cross sections for ionization of K, L, and M shells of atoms by impact of electrons and positrons with energies up to 1 GeV: Analytical formulas,” *At. Data and Nucl. Data Tables* **97**, 186 (2011).
- [4] X. Llovet, C. J. Powell, A. Jablonski, and F. Salvat, “Cross Sections for Inner-Shell Ionization by Electron Impact,” *J. Phys. Chem. Ref. Data* **43**, 013102 (2014).
- [5] J. H. Scofield, “Theoretical photoionization cross sections from 1 to 1500 keV,” Technical Report UCRL-51326 (Lawrence Livermore Laboratory, Livermore, California, 1973).
- [6] T. A. Carlson, *Photoelectron and Auger Spectroscopy* (Plenum Press, New York, 1975).
- [7] G. P. Williams, “Electron Binding Energies of the Elements,” in W. M. Haynes and D. R. Lide, editors, *CRC Handbook of Chemistry and Physics*, 92nd edition, Section 10, pp. 221–226 (CRC Press, Boca Raton, 2011).
- [8] S. T. Perkins, D. E. Cullen, M. H. Chen, J. H. Hubbell, J. Rathkopf, and J. Scofield, “Tables and graphs of atomic subshell and relaxation data derived from the LLNL evaluated atomic data library (EADL), $Z = 1\{100$,” Technical Report UCRL-ID-50400 (Lawrence Livermore National Laboratory, Livermore, California, 1991).
- [9] R. D. Deslattes, E. G. Kessler, P. Indelicato, L. de Billy, E. Lindroth, and J. Anton, “X-ray transition energies: new approach to a comprehensive evaluation,” *Rev. Mod. Phys.* **75**, 36 (2003).
- [10] J. A. Bearden, “X-ray wavelengths,” *Rev. Mod. Phys.* **39**, 78 (1967).
- [11] M. H. Chen, B. Craseman, and H. Mark, *Phys. Rev. A* **27**, 2989 (1983), and earlier papers.
- [12] J. H. Scofield, *Phys. Rev.* **179**, 9 (1969).
- [13] J. H. Scofield, *At. Data Nucl. Data Tables* **14**, 121 (1974).
- [14] J. H. Scofield, in *Atomic Inner Shell processes*, B. Craseman, ed. (Academic Press,

New York, 1973), Chap. VI.

- [15] S. Hüfner, *Photoelectron Spectroscopy: Principles and Applications* (Springer-Verlag, Berlin, 1995).
 - [16] G. Wendin, *Breakdown of the One-Electron Picture in Photoelectron Spectra, Structure and Bonding*, Vol. 45 (Springer-Verlag, Berlin, 1981).
 - [17] J. A. Bearden and A. F. Burr, "Reevaluation of x-ray atomic energy levels," *Rev. Mod. Phys.* 39, 125 (1967).
 - [18] W. Lotz, "Electron binding energies in free atoms," *J. Opt. Soc. Am.* 60, 206 (1970).
 - [19] C. J. Powell, "Recommended Auger parameters for 42 elemental solids," *J. Electron Spectrosc. Relat. Phenom.* 185, 1 (2012).
 - [20] A. Naumkin, A. Kraut-Vass, S. W. Gaarenstroom, and C. J. Powell, NIST X-ray Photoelectron Spectroscopy Database, NIST SRD 20, Version 4.1, National Institute of Standards and Technology, Gaithersburg, MD, 2012; available at <http://srdata.nist.gov/xps>.
-

APPENDIX A

UNCERTAINTIES OF CROSS SECTIONS FROM THE DATABASE

Llovet *et al.* [4] evaluated calculated and measured cross sections for K-shell, L-subshell, and M-subshell ionization by electron impact. They surveyed a number of theories used to calculate ionization cross sections with emphasis given to the formulation of Bote and Salvat [1]. These authors showed that calculations could be made with the plane-wave Born approximation for overvoltages greater than 16 and with the distorted-wave Born approximation for lower overvoltages. This approach is very attractive since the calculations can be made for any neutral atom and for a wide range of incident electron energies. Bote and Salvat [1] used this approach to calculate K-shell and L- and M-subshell ionization cross sections for all atoms from hydrogen to einsteinium and for incident electron energies from threshold to 1 GeV. Similar calculations were made for incident positrons. Bote *et al.* [2,3] then fitted the calculated cross sections with two analytical formulae, one for overvoltages less than 16 and the other for overvoltages greater than 16, and determined the fit parameters for each element and ionized shell or subshell. The fitted cross sections represented the calculated cross sections to about 1 %.

Llovet *et al.* [4] made graphical comparisons of measured K-shell, L-subshell, and M-subshell ionization cross sections with the corresponding cross sections from the Bote *et al.* [2,3] formulae. Similar comparisons were made of measured $L\alpha$ x-ray production cross sections with x-ray production cross sections obtained from the Bote *et al.* L_3 -subshell ionization cross sections and needed relaxation data from the Evaluated Atomic Data Library [8]. These comparisons showed the degree of consistency of measurements by different authors with different measurement techniques as well as the degree of consistency with the Bote *et al.* values.

Llovet *et al.* [4] then performed a more quantitative evaluation of the measured and calculated cross sections. They selected elements for which there were at least three (for K-shells) or two (for L- and M-subshells) mutually consistent sets of cross-section measurements. For these elements, they identified sets of experimental data for which the cross sections showed a satisfactory degree of consistency with each other and for which the cross sections, as a group, varied with incident electron energy in satisfactory agreement with theory. They used the calculated cross sections of Bote *et al.* [2,3] as a guide to the expected energy dependence for each element. Use of the calculated cross sections was critical in this evaluation because the authors could thereby establish consistency (or otherwise) of data sets in non-overlapping energy ranges. Their selection of data sets was, of necessity, qualitative since some data sets were sparse or in non-overlapping energy ranges.

Llovet *et al.* [4] were able to make a more quantitative analysis by determining percentage deviations between measured cross sections in the selected data sets and the corresponding calculated cross sections. They examined plots of these percentage deviations as a function of overvoltage to assess whether there were any systematic trends. Llovet *et al.* then determined root-mean-square (RMS) percentage deviations and mean percentage deviations for each element. Finally, they examined plots of these deviations as a function of atomic number, Z , to determine whether there were any systematic trends.

For K-shell ionization cross sections, Llovet *et al.* identified 26 elements with sets of measured cross sections that satisfied their selection criteria. The percentage deviations for these elements did not vary significantly with overvoltages between 1.02 and 2×10^5 , and the average values of these deviations and of the RMS percentage deviations did not vary significantly with atomic number from $Z = 6$ to $Z = 83$. For all of the selected elements, the average RMS deviation between the measured and calculated cross sections was 10.3 %, while the average deviation was -1.9 %. Calculated cross sections from the Bote *et al.* [2,3] formulae for H and He were also found to be consistent with the measured cross sections for overvoltages larger than 16. They therefore inferred that the Bote *et al.* formulae should also be valid for Li, Be, and B at similar overvoltages.

Llovet *et al.* [4] identified seven elements for which there were two or more sets of total L-shell ionization cross-section measurements and one element (Xe) for which there were two sets of L_3 -subshell cross-section measurements that satisfied their selection criteria. The individual percentage deviations did not depend significantly on atomic number (between Ag and U) or on overvoltage (between 1.02 and 6×10^5). For all of the selected elements, the average RMS deviation between the measured and calculated cross sections was 15.0 %, while the average deviation was -3.1 %.

There were only three elements with two or more sets of M-shell ionization cross sections that satisfied the evaluation criteria of Llovet *et al.* [4]. The individual percentage deviations did not depend significantly on atomic number (between Au and U) or on overvoltage (between 23 and 10^5). For these elements, the average RMS deviation between the measured and calculated cross sections was 23.5 % while the average deviation was 8.2 %.

Llovet *et al.* [4] identified eight elements for which two or more sets of measured $L\alpha$ x-ray production cross sections that satisfied their evaluation criteria. The individual percentage deviations between measured and calculated $L\alpha$ x-ray production cross sections did not vary significantly with atomic number (between Gd and Bi) or L_3 -subshell overvoltage ratio (between 1.02 and 6×10^3). The average RMS deviation between the measured $L\alpha$ x-ray production cross sections and the cross sections calculated from the Bote *et al.* formulae (and needed atomic data) was 10.6 %, while the average deviation was -7.3 %.

Llovet *et al.* [4] found that the overall average RMS deviation between the measured and calculated cross sections was 10.9 % and the overall average deviation was -2.5 %. This degree of agreement between measured and calculated ionization and x-ray production cross section was believed to be very satisfactory given the difficulties in making absolute cross-section measurements. It is not surprising that there were larger deviations between measured L- and M-subshell ionization cross sections and the corresponding calculated values than for K-shell cross sections since there are additional uncertainties associated with the needed atomic data [8].

The average RMS percentage deviations in the preceding five paragraphs provide measures of the one-standard-deviation uncertainty of ionization cross sections from the database. Users should select the relevant uncertainty value that corresponds to the particular cross section of interest. The fact that the average percentage deviation in the various comparisons was typically much less than the RMS deviation indicates that there were no significant sources of residual systematic uncertainty between the measured and calculated cross sections.

Although Llovet *et al.* [4] specified that the overvoltage should be greater than 1.02 for reliable use of the Bote *et al.* formulae, they also indicated that the incident energy should also be a minimum of 50 eV larger than the threshold energy for ionization. This extra restriction was added in order to avoid effects due to post-collision interactions in free atoms or molecules and to so-called final-state or screening effects in solids.

Perkins *et al.* [8] provided the following information on uncertainties of data in their Evaluated Atomic Data Library. Based on the calculations of Chen *et al.* [11], the Auger (non-radiative) widths for an inner-shell vacancy are known to better than 15 % if the inner shells do not decay by Coster-Kronig or super-Coster-Kronig transitions; for these transitions, the widths can be too large by a factor of two. These uncertainties directly affect the competition between radiative and non-radiative yields (*e.g.*, the fluorescence yield). The K- and L-shell radiative rates from Scofield's calculations [12] are accurate to about 10 %. For outer subshells with transitions under 100 eV, inaccuracies of 30 % would not be surprising.

APPENDIX B

SELECTION OF INNER-SHELL BINDING ENERGIES [4]

We give guidance here on the selection of inner-shell binding energies that are needed in calculations of ionization cross sections from the Bote *et al.* formulae [2,3]. These cross sections depend on the overvoltage U , the ratio of the incident electron energy to the binding energy (BE) of the shell or subshell of interest, as well as on parameter values specific to the particular element and shell [2,3].

The BE is usually defined as the minimum energy required to remove an electron in a particular shell or subshell of an atom or molecule to a free or unbound state. For a solid, the electron of interest is removed to infinity, *i.e.*, a large distance from the solid. For atoms and molecules, BEs are conveniently measured with respect to the vacuum level (*i.e.*, the potential at a large distance from the atom or molecule), while for solids BEs are conveniently measured with respect to the Fermi level. In principle, it might be thought that BEs for a solid plus a work function should be the same as the corresponding BE for an atom or molecule, but this simple relationship breaks down due to a number of additional considerations.

The BE definitions given here have an important qualifier, namely that all other electrons in the atom, molecule, or solid are assumed to remain in their original states. It is well known, however, that removal of one electron from an atom, molecule, or solid will cause relaxation of other orbitals [15]. X-ray photoelectron spectroscopy (XPS) is a common method for the determination of BEs. The act of photoionization in XPS generally causes so-called electron shake-up and shake-off in isolated atoms and molecules (*i.e.*, excitation of a valence electron to unoccupied discrete states or to the continuum). For solids, one sees so-called satellite lines due to discrete excitations from the valence band to some unfilled states or to intrinsic collective excitations (plasmons). The XPS lines of conductors also become asymmetrical due to the intrinsic excitation of electron-hole pairs. There are both “chemical shifts” of photoelectron lines for an atom in different chemical states in a molecule or solid and “surface or interface” shifts of photoelectron lines for an atom in a surface or interface atomic layer compared to its bulk. The simple one-electron picture on which the BE definitions are based breaks down for some atoms and shells. Strong many-electron effects are observed in 4s, 4p-like holes in Cd to Gd and 5s, 5p-like holes in Bi to Pu due to so-called giant Coster-Kronig fluctuations and decays [16].

Finally, the work function of a solid is a surface property, and different crystal faces of the same solid generally have different work functions. The work functions also vary with adsorption of molecules on the surface, and with reactions such as oxidation. Work functions typically vary between 2 eV and 6 eV, and it is reasonable to assume an average value of 4 eV when comparing BEs of atoms and solids; nevertheless, BE differences of up to 2 eV could occur due to work-function variations among different solids. While we have commented here on the determination of BEs by XPS, similar effects need to be considered with other methods for the determination of BEs (*e.g.*, x-ray absorption spectroscopy and electron energy-loss spectroscopy).

We now comment on three useful compilations of BEs. The first of these is the 1967 compilation of Bearden and Burr [17]. At least one BE for most elements was determined by

XPS, and other BEs were calculated from BE differences obtained from x-ray emission and absorption spectra. Many if not most of the XPS measurements at that time had been made in instruments that did not have ultrahigh vacua. As a result, many of the “elemental” samples were probably oxidized or had other surface compounds and impurity layers. These “chemical” effects could lead to shifts or errors of several eV or more in the published BEs.

A second comprehensive Table of BEs for atoms is included in a 1975 book by Carlson [6]. This compilation is based mainly on the work of Lotz [18] who lists BEs for free atoms. The latter work is based in large part on the Bearden and Burr [17] tabulation (with work-function additions for solids to refer the BEs to the vacuum level, and some smoothing).

The third BE compilation was made by Williams [7]. While this compilation is not as complete as those of the other two compilations, it contains more recent BE measurements made by XPS. In addition, many (though not all) of the BEs in the Williams compilation are based on XPS measurements with samples prepared in ultrahigh vacua. We therefore expect that these BEs to be generally more reliable than those in the Bearden and Burr tabulation (and the derivative Lotz and Carlson tabulations). We also note that calibration reference data and BE-calibration procedures for XPS instruments did not become available until around the 1990s. Refined BEs for some 50 elemental solids have been published by Powell [19].

Comparisons of BEs in the Carlson and Williams compilations show that a large majority of the BE differences were less than 3 eV. Differences of this magnitude could reasonably be expected on account of chemical shifts for some measurements (due to some early measurements probably being made on oxidized samples), uncertainties of the work-function data, or to inadequate calibrations of the BE scale for some measurements. When larger differences occur, these can be resolved in most cases by further comparisons with BEs for many atoms, molecules, and solids in the NIST XPS Database [20]. We note, however, that most BEs in this database were measured in XPS instruments with Al K α x-ray sources. As a result, these BEs are typically less than about 1.4 keV.

We recommend that ionization cross sections for atoms and molecules be calculated with BEs from the Carlson compilation while similar calculations for solids should be made with BEs from the Williams tabulation. If the desired BEs are not listed in the latter tabulation, BEs from the Carlson compilation can be used (but with a reduction by the average work-function correction of 4 eV). Use can also be made of BEs for atoms, molecules, and solids in the NIST XPS Database [20]. Small differences of BEs from the different sources (*e.g.*, less than 3 eV) will generally have negligible effects on calculated cross sections except for BEs less than about 500 eV and incident energies close to the ionization threshold (*e.g.*, $U < 3$) where the cross sections vary rapidly with energy.

APPENDIX C

CONTACTS

If you have comments or questions about the database, the Standard Reference Data Program would like to hear from you. Also, if you have any problems with the CD-ROM or downloading the database files, please let us know by contacting:

Mr. Adam Morey
Standard Reference Data Program
National Institute of Standards and Technology
100 Bureau Drive, Stop 2310
Gaithersburg, MD 20899-2310
Internet: data@nist.gov
Phone: (301) 975-2200

If you have technical questions relating to the data, contact:

Dr. Cedric J. Powell
National Institute of Standards and Technology
100 Bureau Drive, Stop 8370
Gaithersburg, MD 20899-8370
E-mail: cedric.powell@nist.gov
Phone: (301) 975-2534

Dr. Francesc Salvat
Facultat de Física (ECM)
Universitat de Barcelona
Diagonal 647
08028 Barcelona
Spain
E-mail: francesc.salvat@ub.edu
Phone: (+34) 93-40-21186
FAX: (+34) 93-40-21174
