PHYSICAL REVIEW VOLUME 139, NUMBER 1A 5 JULY 1965

Gryziński Electron-Impact Ionization Cross-Section Computations for the Alkali Metals*

ROBERT H. MCFARLAND
Lawrence Radiation Laboratory, University of California, Livermore, California

(Received 20 January 1965)

The absolute cross sections for ionization by electron impact have been calculated by classical theory for the alkaline metals. The results are in agreement with earlier experimental measurements.

INTRODUCTION

THE absolute ionization cross section caused by electron impact was computed for lithium by McDowell and Peach[1] in 1961 using Born-approximation scattering theory. In the same year Drawin[2] modified classically derived equations of Thomson,[3] Elwert,[4] and others[5,6] to derive an empirical relationship which was used to calculate lithium cross sections for energies extending to 130 eV. Peach and McDowell[7] improved their lithium calculations by including $l=2$ contributions, but indicated that contributions of larger l values could be appreciable. In the meantime, classical theory developed by Gryziński[8,9] was used to approximate a number of experimental ionization measurements.

From theory developed by Gryziński for ionization by electrons, the ionization cross section may be determined by

$$Q^k(E,U_k)=\frac{6.56\times10^{-14}}{U_k^2}g(E/U_k),$$

$$g(\chi)=\frac{1}{\chi}\left(\frac{\chi-1}{\chi+1}\right)^{3/2}\left[1+\tfrac{2}{3}\left(1-\frac{1}{2\chi}\right)\ln(2.7+(\chi-1)^{1/2})\right]. \tag{1}$$

In this representation U_k is the ionization potential in electron volts of the ionization process being considered. E is the energy (eV) of the impacting electron.

Since the expression cited above gives the value of the cross section for an individual electron in the target atom as a function of the energy of the impacting electron, the atomic cross section is

$$Q_{\mathrm{atom}}{}^{+}(E)=\textstyle\sum_k N_k Q^k(E,U_k). \tag{2}$$

Thus one must sum over all the closed shells of the atom as well as the valence electrons. N_k is the number of electrons requiring a given minimum energy for removal from the atom. Relating this to the alkali metals, however, one seldom need consider the closed shells, except for the outermost one, as the U_k^2 term causes these contributions to be orders of magnitude less than for the valence electron.

Information concerning ionization potentials for the valence electron can be readily obtained from many sources. On the other hand, information concerning the energy required for removing electrons from closed shells is less readily available. X-ray absorption-edge data,[10,11] which approximate the desired values, may be in error by as much as 20 eV. Excitation-level data,[12] which include excited states and ionization limits arising from excitation of inner shell electrons, are available for some atoms. As an example, absorption-edge data cite 3 eV as the energy necessary to remove a P electron from the first closed shell of cesium while excitation levels due to excitation of this electron are reputed[12] to have ionization limits at 17.2, 17.25, 19.0, and 19.1 eV. Potassium $M_{\mathrm{II,III}}$ absorption edges are cited as approximating 16 eV, while the lowest excited states of the M shell, P electrons have been observed at 18.7 and 19 eV. Thus, the ionization limit must lie above 19 eV. Energies selected for use in computing partial cross sections as well as the number of effective electrons are shown as a part of the labeling of the curves which are to follow.

RESULTS AND DISCUSSION

Figures 1–5 exhibit the partial and total cross sections for the more loosely bound electrons as computed from Gryziński theory and earlier experimental work.[13–15] For lithium the comparison between this calculation and the previous experimental work is excellent. Drawin's[2] early prediction of the cross section over the range 0 to 134 eV is also within the experimental error of the absolute cross-section measurements.

The more complex atoms—sodium, potassium, rubidium, and cesium—are not as easily analyzed as lithium

---

[*] Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] M. R. C. McDowell and G. Peach, Phys. Rev. **121**, 1383 (1961).

[2] H. W. Drawin, Z. Physik **164**, 513 (1961).

[3] J. J. Thomson, Proc. Cambridge Phil. Soc. **23**, 839 (1927).

[4] G. Elwert, Z. Naturforsch. **7a**, 432 (1952).

[5] D. L. Webster, W. W. Hansen, and F. B. Duvenbeck, Phys. Rev. **43**, 839 (1933).

[6] N. Margulis, Physik. Z. Sowjetunion **5**, 407 (1934).

[7] G. Peach and M. R. C. McDowell, *Atomic Collision Processes* (North-Holland Publishing Company, Amsterdam, 1964), p. 277.

[8] M. Gryziński, Phys. Rev. **115**, 374 (1959).

[9] M. Gryziński, *Atomic Collision Processes* (North-Holland Publishing Company, Amsterdam, 1964), p. 226.

[10] D. Strominger, J. M. Hollander, and G. T. Seaborg, Rev. Mod. Phys. **30**, 594 (1958).

[11] J. A. Bearden, U. S. Atomic Energy Commission, Division of Technical Information Extension, Oak Ridge, Tennessee, Report No. NYO-10586, 1964 (unpublished).

[12] C. E. Moore, Natl. Bur. Std. (U. S.), Circ. No. 467, Vol. I, 1949; Vol. II, 1952; Vol. III, 1958.

[13] J. T. Tate and P. T. Smith, Phys. Rev. **46**, 773 (1934).

[14] G. O. Brink, Phys. Rev. **127**, 1204 (1962).

[15] R. H. McFarland and J. Kinney, Phys. Rev. **137**, A1058 (1965).

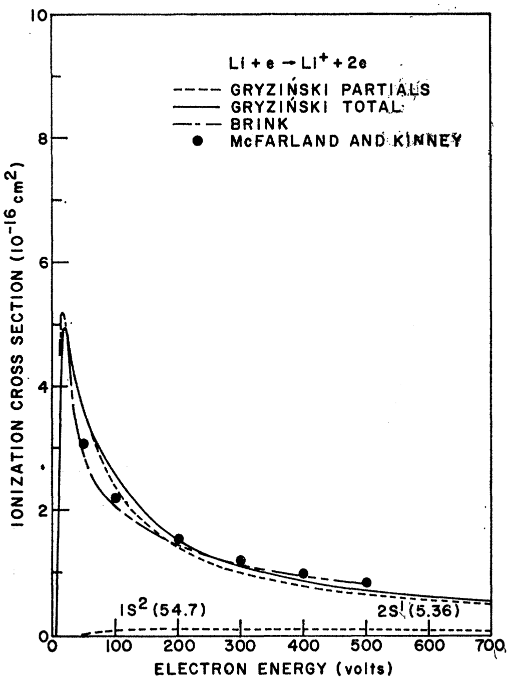

FIG. 1. The electron-impact ionization cross section versus electron energy curves as computed by Eqs. (1) and (2) for lithium. Note that the contribution of electrons with the same *N* and *l* values are labeled as partial Gryziński contributions. The number of electrons effective, the shell, and the ionization potential are to be found adjacent to each partial curve.

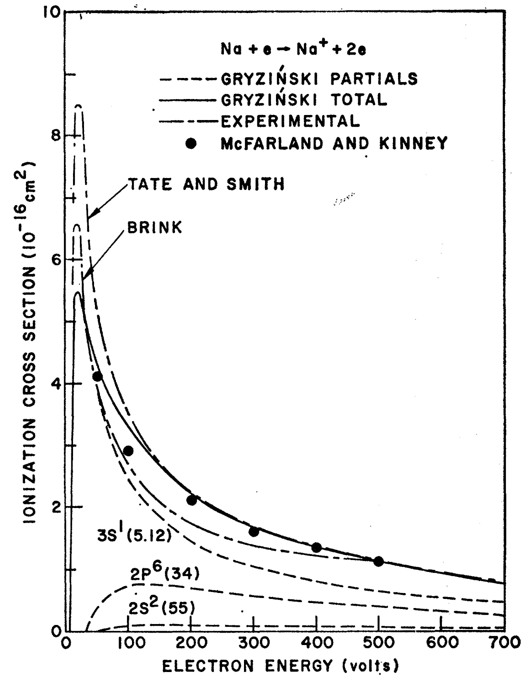

FIG. 2. The electron-impact ionization cross section versus electron energy for sodium.

or hydrogen,[9] or helium,[9] simply because it is difficult to obtain effective ionization potentials of the closed-shell electrons. The contribution of the closed-shell electrons to the total cross section is interesting in terms of the manner in which they may distort the logarithmic portion of the curve. Further, the double peaking observed in these atoms may be explained qualitatively in this fashion. Previous explanations for this effect for these and other atoms[16,17] have been in terms of auto-ionization from specific auto-ionization states.

Obviously auto-ionization must be effective, but one would expect specific levels to have a small and energy-resonant effect as observed by Kaneko[18] for Mg^+. This is due to auto-ionization's being first an excitation effect. On the other hand an infinite number of excitation states leading to auto-ionization exist that terminate in specific ionization states. These are well defined for rubidium and cesium.[12]

As in previous calculations, the Gryziński theory seems to fit the experimental data most poorly in the lower energy range. This is also the energy region in which the experimental error is the largest. As in sodium, there is as much disagreement among experimental results as there is between results and theory. The agreement of theory with earlier absolute measurements by McFarland and Kinney is within the expected experimental error of 10%, except for cesium where, as indicated previously, there appears to be some lack of knowledge concerning the relative abundance of the various species of ions.

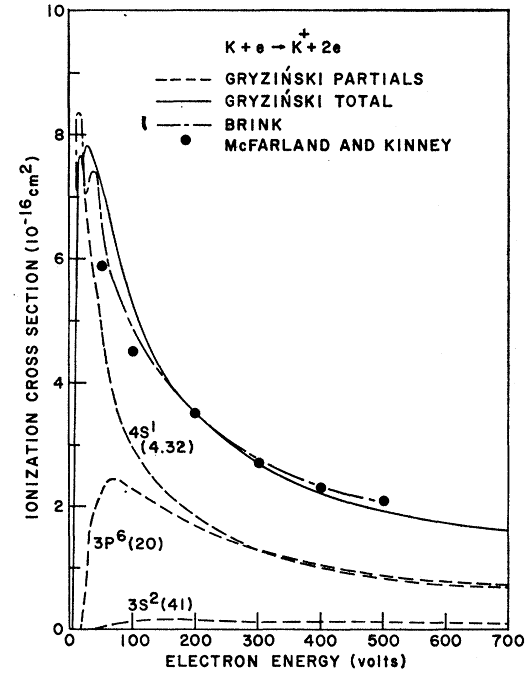

FIG. 3. The electron-impact ionization cross section versus electron energy for potassium.

---

[16] W. M. Hickam, Phys. Rev. **95**, 703 (1954).
[17] N. C. Blais and J. B. Mann, J. Chem. Phys. **33**, 100 (1960).
[18] Y. Kaneko, J. Phys. Soc. Japan **16**, 2288 (1961).

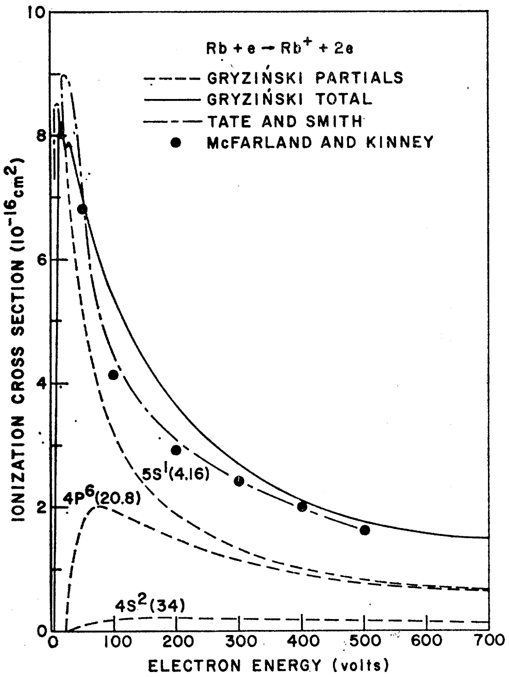

FIG. 4. The electron-impact ionization cross section versus electron energy for rubidium.

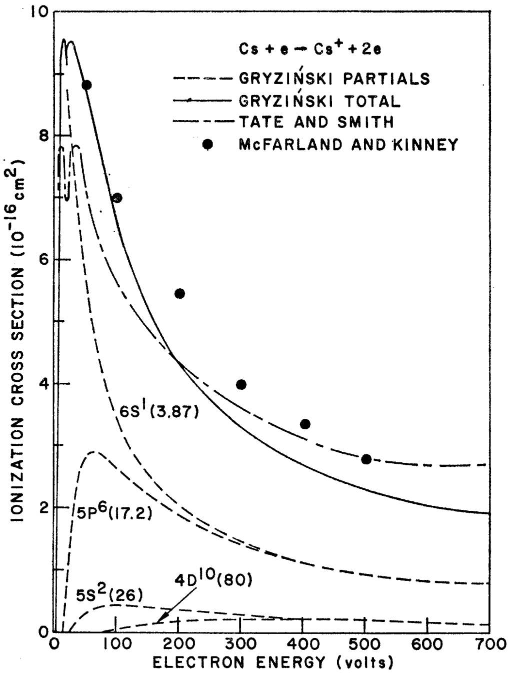

FIG. 5. The electron-impact ionization cross section versus electron energy for cesium.

In conclusion, one may observe that the Gryziński computations yield electron impact ionization cross sections in complex atoms that agree with experimental results, particularly in the higher energy ranges. Further, Gryziński has shown that his calculations agree with experimental work on electron impact ionization involving H, H_2, He, and Ar. In at least the case of H, there is agreement also with Born-approximation-theory calculations.

To the extent that one can assume that these comments are relevant, the Gryziński method provides a much needed simple and quick approach to the problem of normalizing relative experimental measurements to absolute values.

At lower energies, one probably should inquire as to which are the more correct, the computed or the experimental values. For many purposes the computed values provide acceptable accuracy.

The agreement between the computational and experimental cross sections for the alkali metals adds further credence to the assumptions inherent in the previous experimental work.[15] These were that the atomic and ionic reflection coefficients of the alkali metals on hot tungsten and oxidized tungsten equal zero. This is particularly interesting as the assumptions have been used in many previous experimental research efforts without specific direct proof.

Note added in proof. Another interpretation of Tate and Smith's ordinates[13] to be proportional to NQ^{++} rather than "a measure of the relative probability of the production of the different ions," leads to adjusted cross-section magnitudes for sodium, rubidium, and cesium. The 50, 100, 200, 300, 400, and 500 electron-volt cross sections become 4.1, 2.9, 2.1, 1.7, 1.45, and 1.3 for sodium, 7.3, 5.3, 4.3, 3.5, 2.85, and 2.5 for rubidium, and 10.1, 8.7, 7.4, 6.25, 5.15, and 4.4 for cesium. The principal effect of this interpretation is to increase the lack of agreement between the calculated and experimental values for cesium.