PHYSICAL REVIEW LETTERS

VOLUME 33 | 16 SEPTEMBER 1974 | NUMBER 12

Photoionization Cross Sections of the Outer s-Subshell Electrons in the Rare Gases*

James A. R. Samson and J. L. Gardner
Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68508
(Received 8 July 1974)

The absolute photoionization cross sections for the outer *ns* subshells of argon, krypton, and xenon have been measured from their respective ionization thresholds to 41 eV as well as at one point near the ionization threshold of neon. The technique of photoelectron spectroscopy was used to determine the ratio of the *s* to *p* photoelectrons. Measurements of the total cross sections and of the magnitudes of multiple-ionization processes allowed an accurate determination of the subshell cross sections to be made.

Photoionization of the outer *s*-subshell electrons in the rare gases provides a sensitive test of atomic theory applied to the photoionization process. Calculations with single-electron wave functions predict that the photoionization cross sections of the outer *s* shells should be extremely low at threshold relative to *p*-shell ionization (less than about 0.5%). The predicted cross sections then start to increase reaching a broad maximum 20 to 30 eV above threshold.[1,2] However, recent calculations, taking into account the interaction of electrons within a subshell and intershell interactions, yield completely different results (random-phase approximation with exchange, RPAE).[3,4] The threshold cross sections are predicted to be at least 20 times larger than the single-electron–model predictions. The RPAE cross sections are then predicted to drop rapidly to approximately zero at 10 to 20 eV above threshold. The purpose of this paper is to present experimental data supporting the random-phase–approximation method.

Recently, Lynch *et al.*[5] have reported experimental results for the photoionization of the 3*s* subshell in Ar. Their data show a minimum in the cross section in agreement with the RPAE theory. However, there is considerable scatter in their data near threshold that does not allow a more precise comparison with theory. Further, the calculated RPAE values with which their data were compared[3] have been significantly modified in the threshold region.[4] We present here for the first time detailed experimental results of the threshold cross sections of the outer *ns* subshells of Ar, Kr, Xe, and a single point for Ne. The technique of photoelectron spectroscopy was used to determine the ratio of *s* to *p* photoelectrons.

Two sets of data are presented. Earlier data,[6] which were obtained with a retarding-potential electron-energy analyzer, have been reanalyzed, corrected for electron scattering in the gas,[7] and corrected for the varying electron angular distribution[2] in the *p* shell (the asymmetry parameter β was assumed to be equal to 2 for *s*-shell electrons near threshold).

The present data were obtained with a cylindrical-mirror electron-energy analyzer that accepted photoelectrons ejected at 54° 44′ with respect to the direction of the photon beam.[8] At this angle there is no collection discrimination caused by the varying angular distribution.[9] In addition the transmission of the analyzer was calibrated to within ± 5% as a function of electron energy for

TABLE I. *ns/np* ratio for the outer *n* shells of the rare gases. Source lines preceded by an asterisk were produced by a condensed spark discharge in neon. The other source lines were produced in a dc glow discharge in He and Ne and a dc arc in Ar.

Source line λ(Å)		ns/np Ratio (%) Xe	Kr	Ar	Ne
243.027	He II	--	--	--	2.1 ± .4
303.786	He II	5.7 ± 1.2	0.6 ± .5	0.9 ± .5	--
379.31	Ne III	--	3.7 ±1.8	5.3 ±1.0	--
406.50	Ne II	0.0 ± .8	3.3 ± .6	5.0 ± .7	--
* 416.198	Ne IV	--	3.2 ± .7	3.3 ± .8	--
446.4	Ne II	2.9 ± .9	3.1 ± .4	--	--
460.73	Ne II	2.4 ± .9	--	--	--
* 469.817	Ne IV	2.7 ± .7	--	--	--
* 501.0	Ne (?)	3.6 ± .9	--	--	--
518.5	Ar II	2.9 ± .7	--	--	--
* {521.742, 521.813}	Ne IV	3.3 ± .8	--	--	--
522.208	He II	2.0 ± .5	--	--	--
* 526.4	Ne (?)	2.7 ± .7	--	--	--

the range 0–28 eV, by using the method described previously.[8] An accelerating/retarding lens system in the analyzer allowed the electrons to be analyzed at a fixed voltage of 3 V. This prevented discrimination, caused by electron-gas scattering, of electrons with originally different energies.

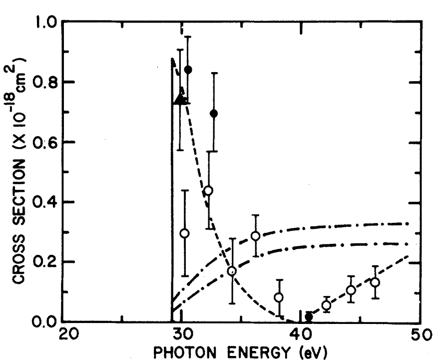

FIG. 1. Photoionization cross sections of the 3*s* subshell of Ar. Theoretical data: dashed line, Ref. 4; dash-dotted line, Ref. 2 (upper curve, dipole length approximation; lower curve, dipole velocity approximation). Experimental data: filled circles, present data; triangle, Ref. 6, corrected; open circles, Ref. 5.

The photoelectron spectra of the rare gases were taken at several discrete wavelengths between 24 and 51 eV. A dc glow discharge in He, Ne, and Ar produced the resonance lines of the neutral and singly ionized atoms.[10] The radiation was then dispersed with a 2-m Vodar grazing-incidence monochromator. An extremely stable scanning voltage source was used to scan the spectra, repetitively, over periods up to 50

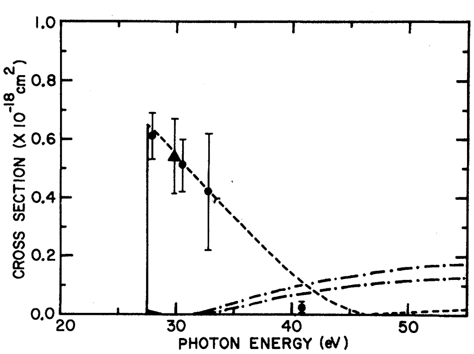

FIG. 2. Photoionization cross sections of the 4*s* subshell of Kr. Lines and data points as in Fig. 1.

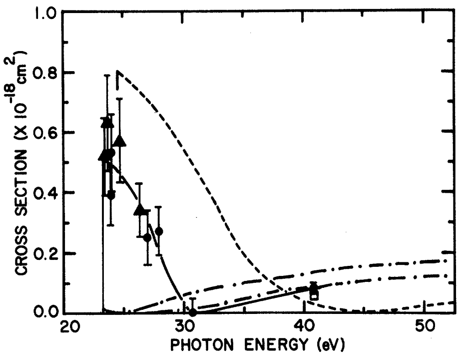

FIG. 3. Photoionization cross section of the 5s subshell of Xe. Lines and data points as in Fig. 1; square, Ref. 14; solid line, suggested experimental cross section.

h. The data were accumulated in a multichannel analyzer. From the data the ratio R, of s to p electrons, was obtained. This ratio is tabulated in Table I. The cross section for photoionization of s-shell electrons σ_s is then given by

$$\sigma_s = \sigma_t R/(1+R), \tag{1}$$

where σ_t is the total photoionization cross section.[11] The effects of double ionization were taken into account at 41 eV in Kr and Xe.[12]

The data for Ar, Kr, and Xe are shown in Figs. 1–3 along with the theoretical calculations.[2,4] The results clearly show the interference effect between the $np^6 \to np^5\,\epsilon d$ transition and the $ns^2 \to ns\,\epsilon' p$ transitions as predicted by Amusia *et al.*[3] The RPAE calculations[3] predict a different situation for Ne. The intershell interaction is weak and, therefore, the 2p subshell does not appreciably affect the 2s photoionization cross section. The form of the curve is similar to the single-particle calculations but the magnitudes of the cross sections predicted by the RPAE calculations are lower. Our single experimental value of $(0.16 \pm 0.03) \times 10^{-18}$ cm^2 near threshold (51 eV) and the data of Wuilleumier and Krause[13] starting at 109 eV are insufficient to verify the lack of interference from the 2p subshell. More experimental data in the threshold region are desirable. The lack of data at high photon energies is simply caused by the low ionization cross sections, weak source line intensities, and discrimination against high-energy electrons by the energy analyzer in the present mode of operation.

The magnitudes of the RPAE results are sensitive to the value of the ns-subshell ionization potential used in the calculations. The RPAE curves for Ar and Kr from Ref. 4, shown in Figs. 1 and 2, respectively, used the experimental ionization potentials. The results are in good agreement with the combined experimental data. For Xe the theoretical ionization potential was used. This accounts for the displacement of the threshold values by 2 eV between the experimental and theoretical curves of Fig. 3. Although the shape of the experimental curve agrees with the RPAE theory, the magnitudes do not. The single value at 41 eV obtained by Kemeny *et al.*[14] has a reported 5s/5p ratio of 0.05. This is to be compared with the present value of 0.057 ± 0.012. Both points have been corrected for double ionization (double-ionization abundance is 20% for Xe at 41 eV).[11]

The data presented here fully support the RPAE-model calculations for the rare gases. However, the discrepancy between theory and experiment for Xe indicates that further refinements are necessary in the RPAE model.

*Research supported by the Atmospheric Sciences Section, National Science Foundation.

[1]J. W. Cooper and S. T. Manson, Phys. Rev. 177, 157 (1969).

[2]D. J. Kennedy and S. T. Manson, Phys. Rev. A 5, 227 (1972).

[3]M. Ya. Amusia, V. K. Ivanov, N. A. Cherepkov, and L. V. Chernysheva, Phys. Lett. 40A, 361 (1972).

[4]M. Ya. Amusia, V. K. Ivanov, N. A. Cherepkov, and L. V. Chernysheva, in *Proceedings of the Eighth International Conference on the Physics of Electronic and Atomic Collisions, Belgrade, Yugoslavia, 1973. Abstracts* (Institute of Physics, Belgrade, Yugoslavia, 1973), p. 581; M. Ya. Amusia, in *Proceedings of the Eighth International Conference on the Physics of Electron and Atomic Collisions, Belgrade, Yugoslavia, 1973. Invited Lectures and Progress Reports* (Institute of Physics, Belgrade, Yugoslavia, 1973), p. 172.

[5]M. J. Lynch, A. B. Gardner, K. Codling, and G. V. Marr, Phys. Lett. 43A, 237 (1973).

[6]J. A. R. Samson and R. B. Cairns, Phys. Rev. 173, 80 (1968).

[7]R. B. Brode, Rev. Mod. Phys. 5, 257 (1933).

[8]J. L. Gardner and J. A. R. Samson, J. Electron Spectrosc. Relat. Phenomena 2, 267 (1973).

[9]J. A. R. Samson and J. L. Gardner, J. Opt. Soc. Amer. 62, 856 (1972).

[10]J. A. R. Samson, *Techniques of Vacuum Ultraviolet Spectroscopy* (Wiley, New York, 1967), Chap. 5.

[11]J. A. R. Samson, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and I. Estermann (Academic, New York, 1966), Vol. 2, p. 117.

[12]J. A. R. Samson and G. N. Haddad, to be published.

[13]F. Wuilleumier and M. O. Krause, Phys. Rev. A 10, 242 (1974).

[14]P. C. Kemeny, R. T. Poole, J. G. Jenkin, J. Liesegang, and R. C. G. Leckey, Phys. Rev. A 10, 190 (1974).