PHYSICAL REVIEW VOLUME 156, NUMBER 1 5 APRIL 1967

Double Electron Ejection Resulting from Photo-Ionization in the Outermost Shell of He, Ne, and Ar, and Its Relationship to Electron Correlation*

THOMAS A. CARLSON
Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received 7 November 1966)

The probability of ejecting two or more electrons by the interaction of an x ray with the outermost shell of He, Ne, and Ar has been investigated. The relative abundances of doubly charged to singly charged ions following x irradiation have been measured with a charge spectrometer. These ratios are essentially constant over the range of x-ray energies from 3 to 8 times the threshold for double ionization. They are, respectively, 0.035, 0.14, and 0.17 for He, Ne, and Ar. Energy spectra for electrons ejected in photo-ionization have been measured with an electron spectrometer. In addition to characteristic photolines, continuum spectra are found, which are related to double electron ejection. The probabilities for double electron ejection as determined from these spectra are in agreement with those obtained by charge spectrometry. The shapes of the continuum spectra are qualitatively similar to those expected for electron shake-off. However, the probabilities for electron shake-off as calculated from single-electron wave functions are much smaller than found experimentally. It is suggested that a many-body solution which explicitly includes electron correlations may be necessary. For example, such a calculation by Salpeter and Zaidi, for the case where one electron goes to the continuum while the other goes to the 2*s* state in the photo-ionization of He, is shown to be in good agreement with experiment. Some results are also presented on the differential cross sections of Ne and Ar for C *Kα* x rays.

I. INTRODUCTION

WHEN a low-energy x ray interacts with an atom, it usually does so by means of the photoelectric effect in which all the energy is converted into the ejection of a single electron.[1] However, if the ejected electron is suddenly removed from one of the inner shells of the atom, there is a change in effective charge experienced by the electrons in the outer shells, which may lead to the simultaneous removal of one of these electrons. This phenomenon, called electron shake-off, has been studied for several atoms[2–5] and in particular for the case of photo-ionization in the *K* shell of neon[2,3]; and the results have been successfully related to a theory based on the sudden approximation. In the study on neon, it was shown that this total intensity for multiple ionization[2,3] agreed well with calculations based on single-electron wave functions, and the shape of the electron energy spectrum[3] was in reasonable agreement with that calculated by Levinger.[6]

A small change in effective charge also is experienced by electrons of the same shell from which the initial electron is removed. Thus, one might expect some shake-off to also occur here. In this paper, I shall give experimental results on the simultaneous ejection as the consequence of photo-ionization of more than one electron from the same shell, namely, the valence shells of He, Ne, and Ar. Qualitatively, the data resemble the electron shake-off phenomenon with regard to the dependence of the extent of ionization on the x-ray energy, and in relation to the shape of the electron spectra; but it will be shown that the observed intensity for extra ionization is in large excess of that computed for electron shake-off based on single-electron wave functions.

It is suggested that a many-body approach that includes electron correlation explicitly may be needed for describing the event in which two electrons are removed from the same shell. A discussion is made of such a calculation with respect to He. Specifically, a comparison is made between theory and experiment for the probability of finding the electron of He$^+$ in the 2*s* orbital as the result of photo-ionization.

II. EXPERIMENTAL

In separate experiments helium, neon, and argon were irradiated with x rays at gas pressures that were sufficiently low that only the consequences of the initial ionization processes were observed. The x-ray energies were too low to create ionization in any but the outermost shell (with the exception of one run on argon). Two sets of experiments were carried out in order to elicit information on the phenomenon of multiple ionization: (1) The relative abundances of the differently charged ions were measured in a charge spectrometer; and (2) the energy spectrum of the ejected electrons was measured with an electron spectrometer.

---

* Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[1] In the energy region in which these studies are carried out inelastic scattering is negligible: for example, E. Storm, E. Gilbert, and H. Israel, Office of Technical Services, Washington, D.C., Report No. LA-2237, 1958 (unpublished).

[2] T. Carlson A. and M. O. Krause, Phys. Rev. **140**, A1057 (1965).

[3] M. O. Krause, T. A. Carlson, and R. K. Dismukes (to be published). See also Bull. Am. Phys. Soc. **11**, 353 (1966).

[4] T. A. Carlson and M. O. Krause, Phys. Rev. **137**, A1655 (1965).

[5] M. O. Krause and T. A. Carlson (to be published).

[6] J. S. Levinger, Phys. Rev. **90**, 11 (1953).

A. Charge Spectrometry

The gas to be studied is allowed to leak into a charge spectrometer, where it is irradiated. The ions formed during this irradiation are accelerated towards the magnetic analyzer, and after passing through the analyzer are counted with an electron multiplier. In this manner a measurement is made of the relative abundances of the different ions that result from the initial photo-ionization. The equipment and experimental procedure have been previously described in detail.[4]

X rays are produced from a tube designed by J. A. Bearden, which employs a tungsten target. The energy of these x rays is determined by the energy of the electrons striking the target and the transmission of the filter. By varying these parameters, it has been possible to carry out the investigation, at least qualitatively, as a function of the energy. In Table I are listed the various x-ray sources, together with an estimate of the average energy that will give rise to photo-ionization as defined by

$$\langle E\rangle=\int_0^{E_{\max}} IT\sigma E dE \bigg/ \int_0^{E_{\max}} IT\sigma dE, \qquad (1)$$

where E is the energy of the x rays in eV, I is the relative intensity of the x rays as determined from Kulenkampff's formula for bremsstrahlung,[7] T is the transmission through the filter, and σ is the cross section[8] for photo-ionization for a given atom. I, T, and σ are functions of E. The value of $\langle E\rangle$ is only approximate since the whole x-ray spectrum is not well established for low-energy x rays, and since the contributions of characteristic lines from W have not been taken into account. However, the values from Eq. (1) afford us, at least, a basis for comparing the results from a variety of x-ray spectra.

B. Electron Spectrometry

An electron spectrometer has been used to measure the photolines and continuum spectra associated with photo-ionization. The spectrometer consists of an electrostatic analyzer, which accepts electrons emitted from the source volume through a series of baffles in a direction perpendicular to the x-ray beam. The electrons that pass through the analyzer are counted with an electron multiplier. A given spectrum is obtained by continually sweeping over a certain energy range by means of applying to the analyzer plates a sawtooth voltage that is synchronized with the channel advance of a multichannel analyzer. A more detailed description of the spectrometer has been given earlier.[9]

One of the experimental objectives of this study has been to keep the background at a minimum, so that the contribution of a continuous spectrum can be clearly seen. One problem has come from the fact that an electron may suffer an inelastic collision with the gas during its traversal from the source volume to the analyzer, and thus appear at slightly lower energies. This effect was corrected for in two ways: (1) by measuring the electron spectra as a function of pressure, and extrapolating the results to zero pressure; and (2) determining, in separate electron-gun experiments, the shape of the energy spectrum that arises when a beam of electrons with an initial fixed energy passes through a given gas, and matching this shape to the spectrum under investigation. Aside from this pressure effect, the background was found to essentially come from only the noise in the electron multiplier. This background was constant over the spectrum and its value was 0.3 counts/min or 4 counts in a channel per day. The x-ray tube is a modified Phillips FAH-20/4 tube, which utilizes a Henke-type target (designed to keep the surface free from tungsten contamination) that was covered with a thick coating of a colloidal suspension of carbon (Aqua-Dag). The x rays passed through a 230 μgm/cm^2 filter of polystyrene. Under these conditions the principal source of radiation should be the CK_α band. Evidence that bremsstrahlung from the carbon target did not play a significant role in determining the energy spectrum of the photoelectron was obtained from the fact that the measured spectrum dropped to

TABLE I. Characteristics of x-ray sources (W target) used in experiments with charge spectrometry. (Energy given in units of eV.)

Run	Atom	Max. voltage	Filter	$\langle E\rangle$[a]	Range of E	
					50%	90%
A	He	3400	450 μg/cm^2 Ni	625	500–700	450–850
B	Ne	840	450 μg/cm^2 Ni	500	400–575	350–725
C	He	1600	225 μg/cm^2 polystrene	290	200–284	125–284[b]
D	He,Ne	800	230 μg/cm^2 polystrene	225	175–250	140–284
E	He,Ne	300	65 μg/cm^2 polystrene	160	110–180	90–235
F	Ar	230	65 μg/cm^2 polystrene	140	120–160	95–200
G	He,Ne	550	20 μg/cm^2 polystrene	130	90–145	80–250
H	He,Ne,Ar	230	20 μg/cm^2 polystrene	110	80–125	60–175
I	He,Ne,Ar	175	20 μg/cm^2 polystrene	85	70–110	55–140
J	Ne	125	20 μg/cm^2 polystrene	72	60–84	50–105

[a] Average energy as defined in Eq. (1).

[b] Most of the remaining 10% was found in the range of 400 to 1000 eV.

---

[7] H. Kulenkampff, Ann. Physik **69**, 548 (1922); H. Kulenkampff and L. Schmidt, *ibid.* **43**, 494 (1943).

[8] J. A. R. Samson and F. L. Kelley, GCA Technical Report No. 64-3-N, Bedford, Massachusetts, 1964 (unpublished).

[9] M. O. Krause, Phys. Rev. **140**, A1845 (1965).

TABLE II. Multiple ionization resulting from x-ray interaction as a function of x-ray energy.

He^{2+}		Ne^{2+}		Ne^{3+}		Ar^{2+}	
$\langle E\rangle$[a]	10^2R[b]	$\langle E\rangle$	10^2R	$\langle E\rangle$	10^2R	$\langle E\rangle$	10^2R
625	3.5±1.2	500	13.6±0.7	500	0.8 ±0.3	140	16 ±1
290	3.6±0.1	225	13.7±0.5	225	0.8 ±0.1	110	15.9±0.6
225	3.5±0.2	160	11.8±0.6	160	0.4 ±0.1	85	13.3±1.5
160	2.9±0.4	130	9.5±0.5	130	0.33±0.04		
130	2.4±0.2	110	8.5±0.2				
110	2.3±0.3	85	6.8±0.3				
		72	4.7±1.0				

[a] Average energy of the x-ray source as given in Table I.
[b] Ratio of the multiply charged ions to the singly charged ions.

background levels at energies where the bremsstrahlung might be expected to have had an effect.

III. RESULTS AND DISCUSSION

A. Charge Spectrometry

In Table II are listed the ratios R of the multiply charged ions to the singly charged ions that result from photo-ionization of the rare gases. These ratios are plotted in Fig. 1 to allow for an evaluation of the probability for multiple ionization as a function of $(\langle E\rangle - I)/I$, where $\langle E\rangle$ is the average energy of the x ray and I is the energy necessary to produce a given doubly (or triply) charged ion. Since we are dealing with a band of x rays, the energy for some of the x rays may fall below I. The dotted line shows values for R' which have been corrected for this fact from the relationship

$$R' = R/(1-a), \qquad (2)$$

where a is the fraction of x rays that lie below the threshold for multiple ionization, as estimated from $\int IT\sigma dE$ as described in Eq. (1).

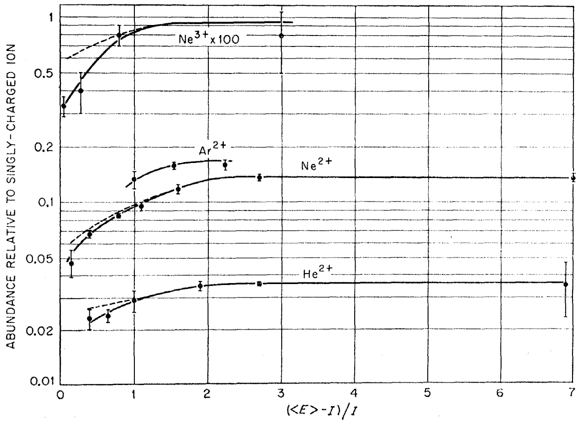

FIG. 1. Relative abundance of multicharged ions produced as the result of photo-ionization in the outermost shell, plotted as a function of energy. Measurements were made with a charge spectrometer. $\langle E\rangle$ is the energy of the x-ray source as defined in Eq. (1), and I is the potential for multiple ionization. The dashed lines are the relative abundance corrected for x rays whose energies lie below the threshold. [See Eq. (2).]

Although the x-ray sources with this large spread in energies do not provide a definitive study of the energy dependence, Fig. 1 suggests that above 2 to 3 times the threshold the extent of multiple ionization remains fairly constant with increasing x-ray energy, but that as one approaches the threshold it begins to drop. Such curves are typical of what one observes in electron shake-off.[2] It is hoped that when monochromatic x-ray sources of reasonable intensities are available (because our target is a gas at low pressure, counting rates are a limiting factor) this experiment can be repeated to bring out the details of energy dependence.

As has been shown earlier,[10] electron shake off as the result of a sudden change in effective charge can be calculated from the following:

$$P_s = 1 - \left[\left| \int \psi_f{}^* \psi_i dr \right|^2 \right]^N - NP_F, \qquad (3)$$

where P_s is the probability that an electron will be removed from a given orbital, ψ_i and ψ_f are single-electron radial wave functions for the initial and final states of these orbitals as obtained from Hartree-Fock solutions,[11] and N is the number of electrons in the orbital. P_F are corrections to filled states, which are physically forbidden by the Pauli principle but must be mathematically accounted for. In photo-ionization the initial configuration is for the atom, and the final configuration is for the singly charged ion with the initial vacancy caused by photoelectron ejection. The values for shake-off include transitions to the excited states as well as to the continuum. In helium, however, good wave functions are available for the excited states as well as for the ground state,[12] and transition probabilities to these excited states have been calculated as well. In Table III theory is compared with experiment. In every case the calculated values for electron shake-off are considerably lower than the experimental data on double ionization. (The discrepancy is even larger if we consider that in the case of Ne or Ar the calculation includes transitions to excited but bound states.) In contrast, the comparison between theory and experiment gave excellent agreement in experiments where the initial electron was ejected from the inner shell and the shake-off occurred in the outer shell.[2,3] The possible reasons for the breakdown between theory and experiment in the present study will be deferred until Sec. III C.

---

[10] For example, A. E. S. Green, Phys. Rev. **107**, 1646 (1957); and Refs. 2 and 4. Note well, in Ref. 2, Eq. (8), there is a misprint. The number 1 should stand outside the brackets as in Eq. (3) of this paper. However, the calculations in Ref. 2 were carried out with the proper formula.

[11] These have been calculated from a code of C. Froese.

[12] The wave functions for the excited state are for hydrogenlike ions. For example, L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 135. The ground state has been taken from L. C. Green, M. M. Mulder, M. M. Lewis, and J. W. Woll, Jr., Phys. Rev. **93**, 757 (1954).

TABLE III. Comparison of experiment with calculation of electron shake-off for probability of double electron emission in the photo-ionization of the outermost shell.

Study	$R\times 100$ Experiment[a]	Theory[b]
He^{2+}/He^{+}	3.6±0.2	1.0
Ne^{2+}/Ne^{+}	14 ±1	4.5
Ar^{2+}/Ar^{+}	17 ±2	3.8

[a] Taken from plateau values at higher energies in Fig. 1.

[b] Calculated from single-electron wave functions. Values for neon and argon also contain contributions to excited but bound states.

B. Electron Spectrometry

In Figs. 2, 3, and 4 are plotted the electron spectra for He, Ne, and Ar arising from x irradiation with the carbon K_α band. The spectra have been corrected for background, pressure effects, relative detection efficiency, and the variation with energy of the width of the energy window, so that the relative probabilities of various parts of the spectrum may be obtained by comparing the integrals: $\int IdE$, where I is the relative intensity and E is the energy. Error bars derived from counting statistics are given at arbitrary points on the spectrum. The energy scale given in the figure is derived from electron gun calibration and related to the most

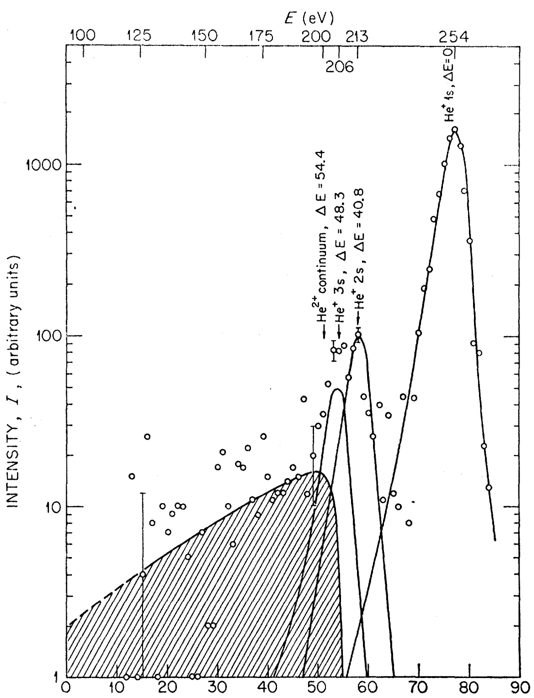

FIG. 2. The electron spectrum resulting from the photo-ionization of He with CK_α x rays. The data have been fully corrected for background and detection efficiency. They have also been corrected for the variation of the width of the energy window so that the integrated areas under the curve, i.e., $\int IdE$, are proportional to the relative probabilities for the different contributions. Because of these corrections, the intensities have been plotted in arbitrary units, although the points are approximately equal to the total number of events observed. Error bars are given for arbitrary points on the spectrum to indicate the uncertainties due to counting statistics. The hatched area indicates the contribution for double electron emission. Arrows point to the energy of the photoelectron corresponding to the ion with the indicated configuration and term value. The values for ΔE have been taken from spectroscopic tables: C. E. Moore, *Atomic Energy Levels* (U. S. Government Printing Office, Washington, D. C., 1949). 1 channel = 2.10 eV.

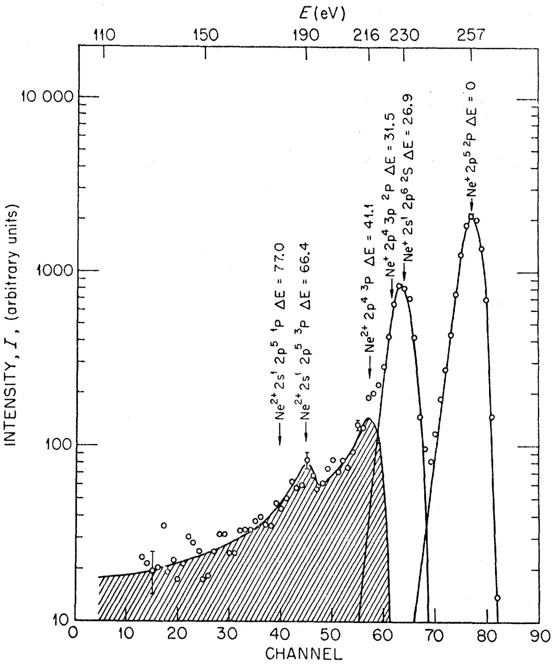

FIG. 3. The electron spectrum resulting from the photo-ionization of Ne. See caption of Fig. 2 for details. 1 channel = 2.05 eV.

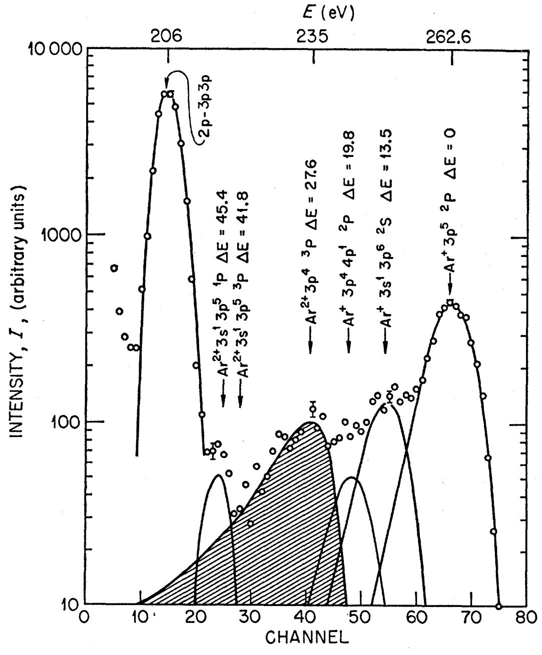

FIG. 4. The electron spectrum resulting from the photo-ionization of Ar. See caption of Fig. 2 for details. 1 channel = 1.10 eV.

energetic photo line whose peak energy is taken as 278.4 eV minus the ionization potential. The values of ΔE are the energy differences from the ground state of the singly ionized rare gas to the indicated excited state, as obtained from spectroscopic tables.[13]

The data given in Figs. 2–4 come from photoelectrons produced by x-ray interaction with the outermost shell of the rare gases (with the exception of the argon spectrum, which also includes a contribution from the LMM Auger process). In addition to the lines associated with transforming all the x-ray energy into removing one s or p electron from the outermost shell, there appears to be a considerable contribution to the spectrum of lower-energy electrons. This portion of the spectrum arises from processes in which a second electron finds itself either in an excited state of the ion or in the continuum. Since energy is conserved, the first electron gives up some of its energy. That is, for a two-electron process

$$h\nu = E_1 + E_2 + I_1 + I_2, \qquad (4)$$

where $h\nu$ is the x-ray energy, E_1 and E_2 are the kinetic energies of electrons one and two, and I_1 and I_2 are the energies necessary for ionization and excitation of the two electrons. $I_1+I_2=I$, where I is the difference in the total energies between the atom and the particular state of the ion following photo-ionization. I shall discuss the data in Figs. 2–4 first, with regard to transitions to the continuum, and then, to excited states.

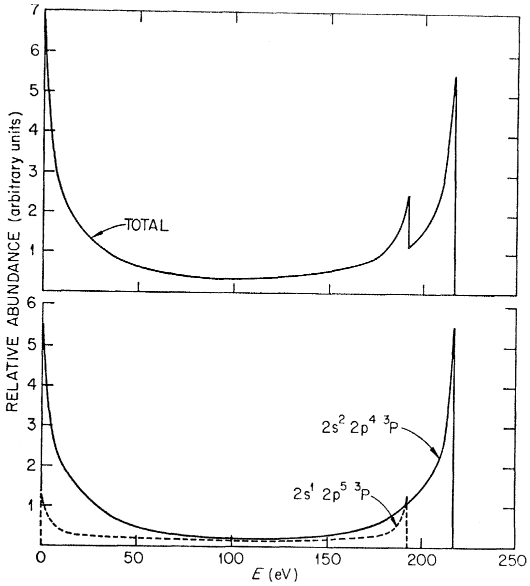

FIG. 5. Electron spectrum for multiple electron ejection in the photo-ionization of Ne as derived from Eq. (4) from data in Fig. 3. At the bottom of the figure are the energy spectra for two electrons in the continuum with the doubly charged Ne left, respectively, in the $2s^22p^4\,{}^3P$ state (solid curve), and the $2s^12p^5\,{}^3P$ state (dashed curve). The plot in the upper part of the figure is the sum of the two contributions.

1. Transition to the Continuum

The hatched areas in Figs. 2–4 indicate a portion of the spectra for electrons that are the result of double electron ejection in the photo-ionization of the outermost shell. The threshold for a given spectrum is the potential for double ionization. What has been measured is the energy spectrum of one of a pair of electrons ejected, the one with the higher energy. Corresponding to this electron, there should exist at a lower energy a second electron. From Eq. (4) we see that for a fixed x-ray energy the two electrons will form a spectrum that is symmetrical about a point midway between zero and I. In Fig. 5, I have generated from the data on neon a complete spectrum, in which the effects of the resolution have been estimated and removed. The total spectrum is made up of two contributions: one, where I = the ionization threshold for removing two $2p$ electrons; and two,[14] where I = ionization threshold for removing one electron from the $2p$ shell and another from the $2s$. Still other small contributions are possible which would increase the complexity of the spectrum (for example, triple ionization, or double ionization plus excitation) but Fig. 5 should be a fair representation of the over-all shape.

Since the hatched areas in Figs. 2–4 represent transitions of two or more electrons to the continuum, while the remainder of the spectrum makes up only single ionization, the ratios of these areas (I have extrapolated the hatched area down to $\frac{1}{2}$ of the threshold for double ionization) should yield results that are in agreement with studies on the charge spectrum. In Table IV, I have compared the ratios of multiple to single ionization

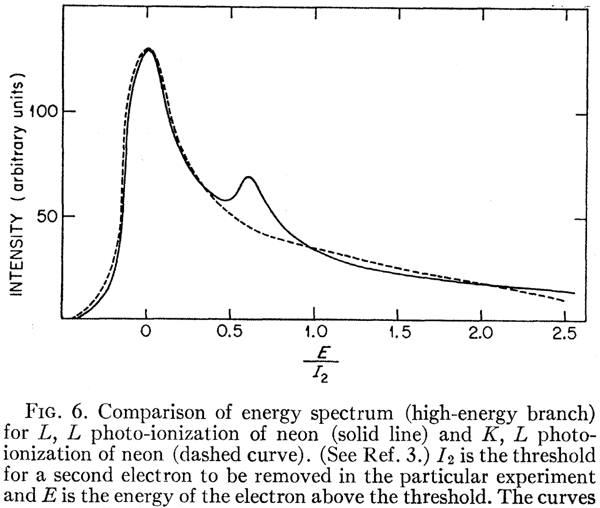

FIG. 6. Comparison of energy spectrum (high-energy branch) for L, L photo-ionization of neon (solid line) and K, L photo-ionization of neon (dashed curve). (See Ref. 3.) I_2 is the threshold for a second electron to be removed in the particular experiment and E is the energy of the electron above the threshold. The curves are normalized at their peaks. Resolution for both studies is approximately the same.

---

[13] C. E. Moore, *Atomic Energy Levels* (U. S. Government Printing Office, Washington, D. C., 1949).

[14] This latter contribution is shown by a peak, in Fig. 3 at 190 eV, which corresponds to leaving the Ne^{2+} in the $2s^12p^5\,{}^3P$ state. In argon a peak occurs close to the energy corresponding to the $3s^13p^6\,{}^1P$ state, but this may be due to some satellite line associated with the Auger spectrum.

for an x ray with energy of 278 eV as taken from charge spectrometry (cf. Fig. 1) and electron spectrometry. The error quoted from electron spectrometry includes consideration of pressure and transmission corrections as well as uncertainties of extrapolating the continuum spectra. The results of the two methods are consistent.

In Fig. 6 the higher-energy branch of the continuum spectrum has been plotted for double electron emission from the L shell of neon, and for a similar study[3] in which K-shell photo-ionization is accompanied by single-electron shake-off from the L shell. The threshold for the latter study is the ionization potential for a $2p$ shell with the configuration $1s^1 2s^2 2p^6$, while in the present case it is for the configuration $1s^2 2s^2 2p^5$. The energy scale is in terms relative to the ionization potentials for the respective experiments. From Fig. 6 one can see that the spectra have essentially the same shape, although the comparison is complicated by contributions from other multiple ionization processes (notably ionization of a $2p$ electron from the configuration: $1s^2 2s^1 2p^6$). Since it was shown in Refs. 2 and 3 that good agreement was obtained between experiment and the theory of electron shake-off, both with regards to the shape of the spectrum and its intensity, one might expect that same agreement would hold in the present study. However, though the shape of the spectra are similar in both studies, one may not conclude that the two phenomena can be treated the same; for it must be remembered, as shown in Table III, that the intensity in the present case where both electrons are removed from the same shell is several times larger than predicted by shake-off calculations.

TABLE IV. Comparison of multiple ionization resulting from x rays of about 278 eV as measured by charge and electron spectrometry.

	$R\times100$	
Study	Charge spect.	Electron spect.
He^{2+}/He^{+}	3.6±0.2	4.5±2
Ne^{2+}/Ne^{+}	14±1	16±3
Ar^{2+}/Ar^{+}	17±2	30±10

2. Transitions to Discrete States

In beta decay it has been found that, if electron shake-off occurs in helium,[15] transitions take place more frequently to the discrete but bound states than to the continuum; but that the reverse is true for the other rare gases.[16] The data from the present experiment seem to reflect the same situation. In Table V are listed the contributions to the discrete states as obtained from data in Figs. 2–4. The energies corresponding to transitions to the first (and in the case of He, also the second) excited states are given in the figures. These values come from solving Eq. (4) for E_2, where $E_1=0$ and I_2 is the excitation energy above the ground state of a singly charged ion. They are based on the assumption that the excited electron will obey selection rules for a monopole transition, while the electron that goes into the continuum follows the conditions for a dipole transition. The opposite might occur, but in any case, the present experiments are unable to make the distinction. Between the first excited state and the onset of the continuum there is the possibility for transitions to still higher excited states. Unfortunately, the limited resolution and the presence of photolines from the s subshells have given us only an approximate evaluation of the role that discrete states play in Ne and Ar. However, in helium the transition to the $2s$ (or $2p$) state is clearly resolved, and a rather large contribution to higher states is also indicated. In fact, the principal problem in helium is to distinguish where the transitions to the excited states leave off, and the continuum begins.

TABLE V. Relative transition probability to excited but bound states following photo-ionization of 278-eV x ray. (Transition to ground state of singly charged ion = 100.)

Excited state	Experimental[a]	Theory
$He^{+}\ 2s$	6±1	1.8[b]; 6.3[b]
$He^{+}\ ns\ (n>2)$	3±1	0.34[c]
$Ne^{+}\ np\ (n>2)$	probably <10	···
$Ar^{+}\ np\ (n>3)$	10±5	···

[a] From spectra in Figs. 2–4 with the assumption that contributions between the energy needed for transitions to the first excited state and the continuum are due to monopole excitation. However, see Sec. III B 2.

[b] Based on calculations of E. E. Salpeter and M. H. Zaidi, Phys. Rev. **125**, 248 (1962).

[c] Based on electron shake-off calculations. [See Eq. (3) and Ref. 12.]

It is of particular value to compare the transition probabilities determined experimentally for the $2s$ state of He with theory. In addition to the shake-off probabilities obtained from single-electron wave functions, described in Sec. III A, calculations were obtained by Salpeter and Zaidi[17] for the oscillator strength functions for photo-ionization leading to the $He^{+}\ 1s$ and $He^{+}\ 2s$ state. That is, they have used Hylleraas-type wave functions, which include electron correlation, to compute the number of times an x ray will eject one electron with or without exciting the ion. The quoted value for the relative cross sections for an x ray with the energy of 278 eV has been obtained by interpolating the results in Table II of Ref. 16. The experimental results are in good agreement with this many-body calculation, but not with the simple calculation on shake-off made in this paper that considers only monopole excitation. Part of the failure of the simple calculation lies in not considering the change in the total cross section. That is, the energy expended in exciting an electron to the $2s$ state, 41 eV, reduces the energy of the photoelectron, which in turn may increase the dipole contribution to the total cross section for photo-ionization plus excita-

---

[15] A. Winther, Kgl. Danske Viedenskab. Selskab, Mat. Fys. Medd. **27**, No. 2 (1952).

[16] See A. E. S. Green, Ref. 10; also T. A. Carlson, Phys. Rev. **130**, 2361 (1963).

[17] E. E. Salpeter and M. H. Zaidi, Phys. Rev. **125**, 248 (1962).

tion, relative to that for photo-ionization, alone. One can estimate this effect on the dipole transition by comparing the measured photoelectron cross section[18] for He at 278 eV and at $278-41=237$ eV. This would increase the cross section by about 60%. One should also consider the possibility for a dipole excitation to the $2p$ state, while the continuum electron goes to the s state[19] (although Salpeter and Zaidi have also neglected this possibility in their calculation).

C. Double Electron Ejection and Electron Correlation

In the preceding section we have seen that the calculation of Salpeter and Zaidi was in much better agreement with experiment than the shake-off calculation based on single-electron wave functions. In their treatment the transition is proportional to the square of the dipole matrix element

$$M_d=\int \psi_f(\mathbf{r}_1,\mathbf{r}_2)(z_1+z_2)\psi_i(\mathbf{r}_1,\mathbf{r}_2)d\tau_1 d\tau_2\,, \tag{5}$$

where ψ_i and ψ_f are the initial- and final-state wave functions for electrons one and two, which include electron correlation for the initial state. If electron correlation is not included, the electron states may be represented by product wave functions,[19] which in the case of double ionization in He yields

$$M_d=2\langle 1s|z|\epsilon_p\rangle\langle 1s|(E-\epsilon)s\rangle\,, \tag{6}$$

where ϵ stands for the continuum states of the p electron, E is the energy above the double ionization, $\langle 1s|(E-\epsilon)s\rangle$ is the matrix element for a monopole transition (i.e., electron shake-off), while the first part of Eq. (6) is the matrix element for a dipole transition. The ratio of the matrix elements for double ionization to single ionization without excitation is

$$R=\frac{\langle 1s|z|\epsilon p\rangle\langle 1s|(E-\epsilon)s\rangle}{\langle 1s|z|\epsilon' p\rangle\langle 1s|1s\rangle}\,. \tag{7}$$

If the energy for the electron going to the s continuum behaves like a simple electron shake-off phenomenon as calculated by Levinger,[6] i.e., is independent of the total energy involved in the ionization and has a distribution with the greatest probability at zero, the following inferences may be made from Eq. (7): (1) Since the probability for a dipole transition is larger for smaller energies,[20] one finds from Eq. (7) that the ratio will be enhanced over values obtained from the sudden approximation, since the shake-off process will remove energy from the photoelectron, i.e., $\epsilon p<\epsilon' p$. However, such an enhancement would be most effective near the threshold, where the fractional change in the photoelectron energy should be the greatest, but would decrease with increasing x-ray energy. As the x-ray energy $\rightarrow\infty$ Eq. (7) reduces to the sudden approximation, i.e.,

$$R=\frac{\langle 1s|\epsilon s\rangle}{\langle 1s|1s\rangle}\,. \tag{8}$$

The data in Fig. 1 do not support such a behavior. (2) In addition, one might expect the greatest relative enhancement for those atoms that require the most energy for a shake-off process, i.e., those atoms that have the highest threshold for double ionization. But the data in Table III do not support this conclusion. Thus, either or both Eq. (7) and the assumption regarding the energy carried away by the s electron do not appear to be in agreement with the data.

Excluding the effect of a change in shielding (electron shake-off), the ejection of two electrons by the dipole interaction with a photon is theoretically forbidden.[21] This is no longer the case when correlation is taken into account. Welton[22] has shown that by including correlation in Eq. (5) one obtains both monopole and dipole contributions to multiple ionization. When electron correlation must be taken into account, the simple picture of shake-off is no longer a valid one, and other elements[23] are required for a complete explanation of multiple ionization. A more searching approach to the calculation of double ionization in He as the result of photo-ionization is currently in progress.[24]

It should be pointed out here that Auger processes in which two electrons are ejected from the outermost shell have also been observed,[25] and, as in the present study, the electron shake-off calculations based on

---

[18] A. P. Lukirskii, I. A. Brytov, and T. M. Zimkina, Opt. i Spektroskopiya 17, 438 (1964).

[19] For example, F. R. Crownfield, Jr., and P. Havas [Bull. Am. Phys. Soc. 9, 402 (1964)] have investigated this approach.

[20] Cross sections for photo-ionization increase with decreasing energy (at least under the conditions where these studies were carried out). See, for example, Ref. 8.

[21] J. L. Powell and B. Crasemann, *Quantum Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1961), p. 420.

[22] To see this, consider that correlation is to be ignored in the final state and is to be taken into account by first perturbation theory in the initial state. The perturbing energy is the difference between the actual electron-electron repulsion and the effective modification of the central potential, which is roughly equivalent to the electronic repulsion in a Hartree-Fock treatment. The matrix element (5) then splits into a lowest-order contribution equal to (6), and a correction which is a sum of an explicit correlation contribution and a contribution due to alteration in the attractive center potential by reason of electron removal (i.e., electron shake-off).

[23] One might, for example, mention the possibility for a direct collision between the outgoing photoelectron with an orbital electron of the same atom. This has been studied in the case of beta decay: R. M. Weiner, Phys. Rev. 144, 127 (1966); E. L. Feinberg, J. Nucl. Phys. (USSR) 1, 612 (1965). The process of direct collision should be energy-dependent, unlike our experimental data, and has been shown to be unimportant relative to shake-off in K photo-ionization of neon (Ref. 2). In any case direct collision is implicity included when electron correlation is taken into account.

[24] W. R. Garrett and F. B. Malik (private communication).

[25] T. A. Carlson and M. O. Krause, Phys. Rev. Letters 14, 390 (1965).

single-electron wave functions gave much lower values than were experimentally observed. Fano[26] has expressed the hope that in the future the various studies on multiple ionization and excitation[27] may be welded together to give a more unified description of the many-body problem in atoms.

IV. DIFFERENTIAL PHOTOELECTRIC CROSS SECTIONS

Aside from the main purpose of this paper, which has been the study of the nature of multiple photo-ionization, the relative intensities for the *s* and *p* photoelectrons in Figs. 3 and 4 may be used to evaluate the differential photoelectric cross sections of Ne and Ar for x rays of energies of about 278 eV. (There is a sparsity of such data in this energy region.) The electrons that are accepted by the spectrometer emerge from a solid angle of 3°, which is perpendicular to the x-ray beam. This means that relative to the total photo-ionization integrated over all angles, this experiment should yield a slightly greater intensity for *s* electrons relative to *p* electrons for the same principal shell.[28] (A measurement of the angular dependence of photo-ionization is anticipated at a later time.) The results are given in Table VI. In addition, the relative cross section of the $2p$ shell in argon has been estimated from the intensity of the Auger line. [This result is only approximate, since it is assumed that (1) the number of vacancies produced in the $2p$ shell by bremsstrahlung is negligible compared to those results for the C $K\alpha$ band, and (2) the intensities compared at right angle to the beam are not greatly different than would be a comparison of the integrated intensities. These effects, however, tend to cancel each other.]

In Table VI are also given the relative cross sections as calculated from a modified Stobbe-Hall formula.[29] A large disagreement is apparent and it cannot be accounted for in terms of the experimental limitations discussed above. In fact, if they are brought into consideration, the discrepancies would in general be even larger. This disagreement is not surprising, however, since calculations based on hydrogenic wave functions, such as used in the Stobbe formula, are not very accurate for the outermost shell of an atom. More recent computations using Hartree-Fock solutions[30] show that good agreement can be obtained between experiment and theory for the cross sections of low-energy photons if good wave functions are used.

TABLE VI. Differential cross sections of Ne and Ar for C $K\alpha$ x rays (278 eV).

	Relative cross sections			
	Ne		Ar	
Shell	Experimental[a]	Theory[b]	Experimental	Theory
$2s$	0.39	0.91	...	...
$2p$	1.00	1.00	11.2	660
$3s$			0.28	0.65
$3p$			1.00	1.00

[a] From electron spectrum, Figs. 3 and 4, including only photo-ionization to ground state of singly charged ion.

[b] Based on modified Stobbe-Hall formula: A. J. Bearden, J. Appl. Phys. **37**, 1681 (1966).

V. CONCLUSION

Experimental data have been obtained on the ejection of two or more electrons as the result of the photoelectron effect in the outermost shell of He, Ne, and Ar. This phenomenon has been shown to qualitatively resemble electron shake-off, but the extent of double ionization is several times larger than that predicted from simple calculations using single-electron wave function. A more sophisticated approach such as a many-body solution which includes electron correlation seems to be necessary in order to give a correct account of this multiple ionization in the outermost shell.

ACKNOWLEDGMENTS

The author would like to thank Dr. W. R. Garrett, Dr. T. A. Welton, and Dr. M. O. Krause of the Oak Ridge National Laboratory; Dr. F. B. Malik at Yale University; Professor U. Fano at the University of Chicago; and Professor P. Havas at Temple University for their helpful discussions with him. He should also like to acknowledge the help of C. W. Nestor at Oak Ridge National Laboratory for computing on the CDC 1604-A computer, the wave functions and overlap integrals used in this paper.

---

[26] U. Fano (private communication).

[27] For example, U. Fano and J. W. Cooper, Phys. Rev. **137**, A1364 (1965); H. W. Schnopper, *ibid.* **131**, 2558 (1963).

[28] For example, see A. H. Compton and S. K. Allison, *X Rays in Theory and Experiment* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1935), p. 581.

[29] A. J. Bearden, J. Appl. Phys. **37**, 1681 (1966).

[30] For example, J. W. Cooper, Phys. Rev. **128**, 681 (1962); Phys. Rev. Letters **13**, 762 (1964).