Atomic Readjustment to Vacancies in the K and L Shells of Argon*

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The relative abundances have been measured for the argon ions that are formed as the result of atomic readjustment to vacancies in the K and L shells of argon. Initial vacancies were produced by x rays, and the ions were analyzed with a magnetic spectrometer, such as that used by Snell and Pleasonton in their work on radioactive rare gases. A new source volume for extracting the ions was used, and is described. Measurements were made of charge spectra resulting from x rays of the approximate energies 17.5, 4.5, 1.5, and 1.0 keV. The spectra obtained with x-ray energies above the K edge of argon bore a close resemblance to that obtained from $^{37}\mathrm{Ar} \rightarrow_{\mathrm{EC}} {}^{37}\mathrm{Cl}$. For comparison with the experimental results each of the charge spectra was computed from knowledge of radiative and Auger transition rates. In addition, calculations were made of the electron shake-off that arises from sudden changes in the effective charge. In general, the agreement between the calculated and the experimental values is good, although there is some evidence that there may be other sources of additional ionization.

INTRODUCTION

THE production of inner shell vacancies in atoms is a common event in nature. For example, these vacancies arise in nuclear decay as the result of electron capture or internal conversion. They also arise from the interaction of γ rays and x rays with matter by means of photoelectron emission. Even charged particles, if they possess sufficient energy, will promote inner shell vacancies. An atom adjusts to an initial hole by filling it with an electron from one of its outer shells. There is a high probability that the energy given up by filling the hole will be carried away by a second electron, which is ejected from the atom, i.e., by an Auger process, and that two new holes will replace the original one. These new vacancies will then be filled by still more electron transitions from higher shells until the atom, now highly ionized, arrives at a state where no more transitions are possible. This whole process has sometimes been called a "vacancy cascade." We have undertaken[1,2] a broad investigation of atomic readjustment to inner shell vacancies by promoting such vacancies with x rays, and measuring the relative abundances of the ions that subsequently form. From knowledge of the over-all ionization we hope to learn about the cascade of Auger processes involved in atomic readjustment and also about secondary methods of ionization, which accompany these cascades, such as electron shake-off.

The earliest experiments designed to study the phenomena of vacancy cascades by means of charge spectrometry were carried out on radioactive rare gases.[3,4] In the first experiment[5] to combine x rays with charge spectrometry, use was made of a spectrometer that measured coincidences between the ion and the various electrons produced in the ionization. In the present study ions are measured without reference to the ejected electrons. The new spectrometer is thus free from the problem of differences in relative collection efficiencies, as experienced with the coincidence method.

This paper presents results on the relative abundances of argon ions and compares these results with calculations based on probabilities for Auger processes and electron shake-off. The small number of transitions possible in the readjustment to an L shell vacancy in argon allows one an easy assignment of the roles played by these transitions. Any extra ionization can then be related to secondary processes. Investigations of the charge spectra resulting from K vacancies in argon are of particular importance because Rubenstein[6] has calculated all the transition probabilities for radiative and nonradiative transitions in argon that are necessary to account for the complete readjustment to an initial K vacancy. Also, the data can be compared with the charge spectrum[3] resulting from electron capture in $^{37}\mathrm{Ar}$, in which the initial vacancy is primarily in the K shell.

EXPERIMENTAL

The general procedure in charge spectrometry is to allow ionization of a gas to take place in what we term the "source volume." Ions formed in this region are extracted and propelled towards an analyzer. After analysis, the ions are accelerated again to insure equal counting efficiencies, and are counted with an electron multiplier. The results are dependent on two conditions. First, collision of the ions with other gaseous atoms or molecules must be negligible. This is achieved by operating at a sufficiently low pressure. Second, ionization resulting from atomic readjustment must be completed before the ions are extracted for analysis. This condition is easily met, since the time for a vacancy cascade is very short, 10^{-13} to 10^{-15} sec, as compared with the time for collection, about 10^{-5} sec.

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[1] T. A. Carlson and M. O. Krause, Bull. Am. Phys. Soc. **9**, 51 (1964).

[2] M. O. Krause and T. A. Carlson, Bull. Am. Phys. Soc. **9**, 51 (1964).

[3] A. H. Snell and F. Pleasonton, Phys. Rev. **100**, 1396 (1955).

[4] F. Pleasonton and A. H. Snell, Proc. Roy. Soc. (London) **A241**, 141 (1957).

[5] M. O. Krause, M. L. Vestal, W. H. Johnston, and T. A. Carlson, Phys. Rev. **133**, A385 (1964).

[6] R. A. Rubenstein, thesis, University of Illinois, 1955 (unpublished).

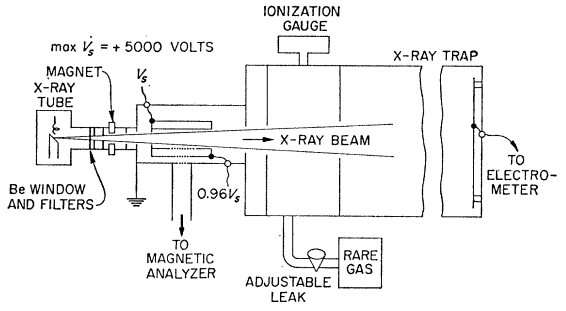

FIG. 1. Source volume for studying the charge distribution of ions produced by x rays.

The source volume used in our present experiments is shown schematically in Fig. 1. After collimation, the x-ray beam passes by the collection plates and is finally stopped at the end of an x-ray trap. Argon, whose purity is better than 99.9%, is let into the source volume by means of an adjustable leak. Ionization is produced along the whole path. Those ions formed in the region of the collection plates are extracted from the source volume by an electric field between the plates of about 4% of the applied voltage, whose total is a maximum of 5000 V. The ions passing through the grids of the lower plates are then accelerated through the remaining potential drop. They emerge from the source volume with energies proportional to their charge, and for a given ion there is an energy spread of about 2%. To insure equal collection efficiencies for the differently charged ions, we have compared their intensities under conditions of equal focusing, viz., the voltage is adjusted inversely proportional to the charge of the ion. In practice it was found that charge spectra taken under conditions when the voltage was held constant were nearly identical to data taken when the voltage multiplied by the charge was held constant.

X rays were obtained from tubes of two different designs. For the more energetic x rays, Machlett tubes were used of the AEG-50 series in which targets of Mo and Ti were incorporated. A full wave rectified voltage was supplied by a G. E. XRD-4 power unit. For x rays of lower energy we used a tube with interchangeable targets of copper and aluminum, designed[7] and built by J. A. Bearden. A dc power supply was used for this tube. The target, the operating voltage, and filters determined the x-ray spectra. Although a monochromator is of course desirable, it does not seem practical because of intensity requirements. However, the choice of the aforementioned three variables gave us reasonable versatility for producing the desired atomic vacancies. In Fig. 2, graphs A and C, we have shown the energy spectra of x rays used for two of our experiments on argon. The spectra have been obtained with a Reuter-Stokes proportional counter. The data for each spectrum have been corrected for escape peaks, and have been compared under conditions of constant resolution (%) and equal counting efficiency. To obtain the relative number of vacancies produced in argon as a function of energy, the intensity, $I(E)$, has been multiplied by the cross section for argon,[8] $\mu/\rho(E)$; the results are displayed in graphs B and D of Fig. 2. The lower energy spectra obtained from the Cu and Al targets (experiments I and II) have not been measured, but we believe that, from the filters employed and from the cross section for argon, x rays giving rise to most of the photoionization have energies in the vicinity of the characteristic L_α lines of Cu or K line of Al. If we include consideration of bremsstrahlung,[9] using Kulenkampff's empirical equation[10] for its shape, we estimate in the case of experiment I that the average energy responsible for ionization is 1.07 keV, and in the case of experiment II, 1.49 keV.

The magnetic analyzer used in the present work is identical to that used earlier for radioactive studies, and more details concerning this part of the spectrometer can be found elsewhere.[3,4] To count the ions which pass through the analyzer, we employed an electron multiplier designed by Johnson.[11] A discussion has previously been given of the problem of obtaining equal counting efficiencies for differently charged ions.[12] In the present study the ions striking the multiplier had energies of at least 9000 eV, so that the multiplier was operated under conditions where differences in the relative counting efficiencies were negligible.

The counting rates for the most abundant ions were the order of 500 counts (c) per min. The background of the electron multiplier was normally about 15 c/min, but was reduced to as low as 2 c/min when a small uncertainty in the counting efficiency could be tolerated. Backgounds were taken under three conditions and cross checked: (1) the collection voltage was turned off, (2) the gas being studied was removed, and (3) the x-ray source was turned off. The x-ray source and the gas pressure were steady, so that no monitoring was necessary. For example, measurements made with an electrometer located at the back of the x-ray trap, showed that the x-ray flux was essentially constant during a run. A charge spectrum was repeatedly measured, and the reproducibility was generally found to be within counting statistics. The errors quoted for the

[7] J. A. Bearden, M. Krause, and W. H. Johnson, Technical Documentary Report ADS-TDR-62-10 (unpublished).

[8] A. H. Compton and S. K. Allison *X Rays in Theory and Experiment* (D. Van Nostrand Company, Inc., New York, 1935), S. J. M. Allen's Tables, pp. 800–806.

[9] For the relative contribution of bremsstrahlung to the characteristic lines we have adjusted some data on Ni taken at low voltages to our experimental conditions: H. Neff, Z. Physik **131**, 1 (1951).

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

[11] C. H. Johnson, F. Pleasonton, and T. A. Carlson, Phys. Rev. **132**, 1149 (1963).

[12] T. A. Carlson, F. Pleasonton, and C. H. Johnson, Phys. Rev. **129**, 2222 (1963).

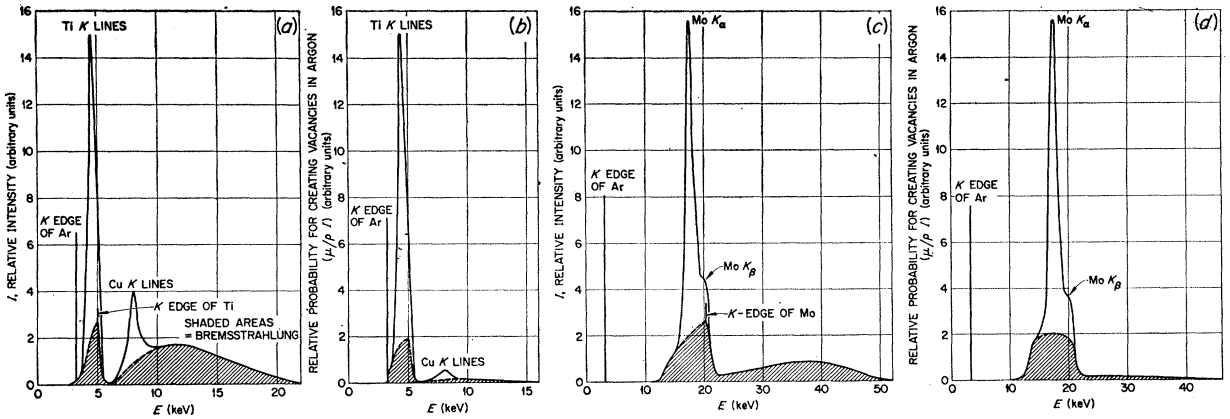

FIG. 2. Graphs A and C are spectra of x rays used respectively in experiments III and IV. Graphs B and D are plots of the relative number of vacancies produced in argon as a function of energy in experiments III and IV, respectivley. The data have been corrected for escape peaks; and the variation with energy of the resolution (%) and counting efficiency has been removed. In experiment III a Machlett AEG-50 tube with a Ti target was operated at 20 keV to produce x rays, which were filtered through 46 gm/cm² of Be and 11 mg/cm² of Ti. In experiment IV a Machlett AEG-50 tube with a Mo target was operated at 52 keV to produce x rays, which were filtered through 230 mg/cm² of Be, 52 mg/cm² of Mo and 34 mg/cm² of Al.

experimental results in this paper are based mainly on counting statistics. The quoted errors for the charge-one ions have been increased, however, because of a small contribution to ionization from stray electrons. This contribution, which is negligible for ions of charge greater than one, has been reduced to a minimum by the use of magnetic deflection following the entrance window for the x rays, and by careful baffling of the x-ray beam.

Only one more experimental problem remains to be discussed, the problem of the pressure effect. It is desirable to work with as high a pressure as possible so as to increase the counting rate. At the same time ion-molecule reactions must not be allowed to influence the results. We have examined the charge spectra as a function of pressure. In Fig. 3 are shown the results of such a study. We have plotted the relative abundances of Ar ions produced by x-ray bombardment as a function of pressure in the source volume. (The pressure in the analyzer is approximately $\frac{1}{5}$ of that in the source volume.) Note that the cross section for ion-molecule reactions seems to increase with the charge of the ion, as expected. There is also some evidence that an ion initi-

TABLE I. Relative abundances of Ar ions formed as a result of photoelectron emission primarily from the L shell. Comparison of experiment with theory.

(% abundance.)

Experiment I. X rays produced by 3.0-keV electrons on a Cu target and filtered through 0.45 mg/cm² of Cu and 0.11 mg/cm² of polystyrene.

Calculation I. Based on the following distribution of vacancies: L_{I} shell, 52.8%; $L_{\mathrm{II,III}}$, 38.1%; M, 9.1%.

Experiment II. X rays produced by 3.0 keV electrons on an Al target and filtered through a 3.4 mg/cm² foil of Al.

Calculation II. Based on the following distribution of vacancies: L_{I} shell, 59.6%; $L_{\mathrm{II,III}}$, 31.3%; M, 9.1%.

A = From Auger processes.
B = From Auger processes and electron shake-off.

Ion	Calculation I		Experiment II	Calculation II	
	Experiment I	A	B		A	B
Ar^{1+}	5.0±1.5	9.1	9.0	4.4±1.5	9.1	9.0
Ar^{2+}	53.3±1.6	39.5	34.4	47.0±1.1	32.8	28.5
Ar^{3+}	32.1±1.2	51.4	49.9	37.0±0.9	58.1	55.2
Ar^{4+}	7.3±0.6	0.0	6.2	9.3±0.6	0.0	6.8
Ar^{5+}	2.2±0.4	0.0	0.4	1.9±0.4	0.0	0.4
Ar^{6+}	0.1±0.2	0.0	0.05	0.4±0.2	0.0	0.06

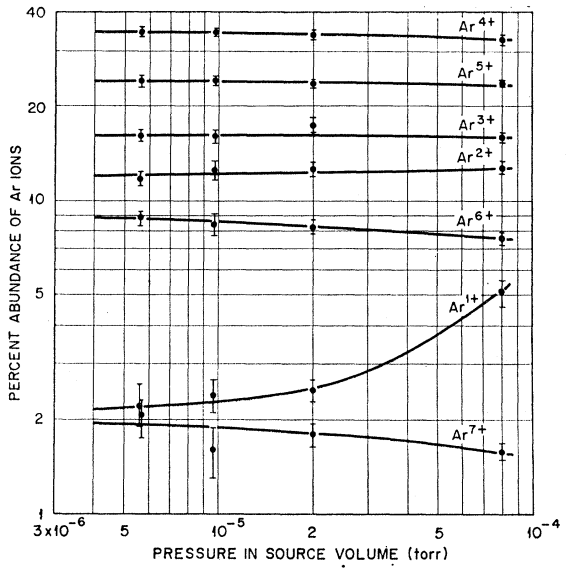

FIG. 3. Dependence of the charge spectrum of Ar ions on the pressure. Initial vacancies have been formed by an x-ray source similar to that employed in experiment III (cf. Fig. 2) with the omission of a Ti filter. The pressure in the analyzer was approximately $\frac{1}{5}$ of that in the source volume.

ally of higher charge may be analyzed, after partial neutralization, as an ion of lower charge. In any case data taken at pressures of less than 2×10^{-5} Torr in the source volume have a negligible pressure effect. When it has been necessary to run at slightly higher pressures, the results have been corrected according to pressure-dependent curves such as given in Fig. 3.

RESULTS AND DISCUSSION

A. L Vacancy in Argon

The relative abundances of argon ions resulting from vacancies produced primarily in the L shell are listed in Table I.

In trying to account for the observed spectra, one finds that the roles played by Auger processes may be easily assigned. Ignoring any contribution from electron shake-off, we find: (1) If a vacancy is created in the M shell, no Auger process can occur,[13] and argon remains singly charged. (2) An $L_{II,III}$ vacancy will be filled by one Auger process, the probability for a radiative transition being negligible, and this results in Ar^{2+}. (3) If the x ray ejects an L_I electron, the most probable charge is three, because the initial vacancy will be filled in nearly every case by a Coster-Kronig transition, which leaves a $2p$ hole that is filled by a second Auger process.[6,14] The first three charges are thus largely determined by the distribution of the initial vacancies.

To obtain the relative probabilities for photoionization in the L_I, $L_{II,III}$, and M shells of argon, we have used the formula given by Stobbe[15] and by Hall[16]:

$$\tau_{LI}/(\tau_{LII}+\tau_{LIII})=E/E_2\left[\frac{(1+3(E_2/E))}{(3+8(E_2/E))}\right], \quad (1)$$

where E is the energy of the x rays and E_2 is the mean energy between the L_I and $L_{II,III}$ shells of argon. From arguments presented earlier in the Experimental section we have used for E, 1.07 and 1.49 keV, respectively, for experiments I and II. The M/L ratio is taken from Jonsson's formula for the L edge,[17]

$$\tau_M/\tau_L=E(M_I)/E(L_I), \quad (2)$$

where $E(M_I)$ and $E(L_I)$ are the binding energies, respectively, for the M_I and L_I shells of argon.

By combining the vacancy distribution with the ionization anticipated from holes in the L and M shell (cf. columns 2, 4, and 6 of Table II), we arrive at the charge spectra as computed for experiments I and II without consideration of electron shake-off. Comparison of these calculations (the A columns in Table I) with the experimental values shows that the vacancy distribution obtained from Eqs. (1) and (2) is in rather poor agreement with experiment. With regard to the relative abundance of Ar^{1+} it is not surprising to find that Jonsson's rule of M ionization, Eq. (2), does not hold too well at energies so far above the L edge. The disagreements between theory and experiment for the ratios of Ar^{2+}: Ar^{3+} are somewhat more disturbing. The small uncertainty in assigning E cannot explain the large discrepancy between theory and experiment. A final appraisal must await theoretical calculations using better wave functions.[18,19]

Table I also lists observed abundances of Ar^{4+}, Ar^{5+}, and Ar^{6+}. These ions must arise from sources of ionization in addition to the initial photoelectron emission and subsequent Auger processes. One such source is electron shake-off. We shall now apply ourselves to the task of calculating this contribution to the charge spectra.

TABLE II. Calculations of the extent of ionization following L and M vacancies in argon.

(% probability for removing n electrons.)

A = From Auger processes.
B = From Auger processes and electron shake-off.

Total no. of electrons removed (n)	Initial vacancy L_I A	L_I B	$L_{II,III}$ A	$L_{II,III}$ B	M A	M B
1	0.0	0.0	0.0	0.0	100.0	99.0
2	2.6	2.3	100.0	87.0	0.0	1.0
3	97.4	86.0	0.0	11.9	0.0	0.0
4	0.0	10.9	0.0	1.0	0.0	0.0
5	0.0	0.7	0.0	0.1	0.0	0.0
6	0.0	0.1	0.0	0.0	0.0	0.0

[13] For an Auger process to occur, the differences between the binding energies of the $3s$ and $3p$ states of neutral argon, $E_{3s}-E_{3p}$, must be larger than the second ionization potential of argon. However, $E_{3s}-E_{3p}$ is only 13.5 eV, while the second ionization potential is 27.6 eV. Cf. C. E. Moore, Atomic Energy Levels, Circ. 467, Natl. Bur. Std. (U. S. Government Printing Office, Washington, D. C.), Vol. 1 (1949), p. 216.

[14] Mehlhorn has shown experimentally that the L_I vacancy in argon is almost always filled by a Coster-Kronig transition. W. Mehlhorn, Z. Physik **160**, 247 (1960).

[15] M. Strobbe, Ann. Physik **6**, 661 (1930).

[16] H. Hall, Rev. Mod. Phys. **8**, 358 (1936). Equation (1) is from Hall and is a factor of 2 higher than Stobbe. Bethe and Salpeter agree with Hall that Stobbe has made an error: H. A. Bethe and E. E. Salpeter, *Encyclopedia of Physics, Atoms I* (Springer-Verlag, Berlin, 1957), Vol. XXXV, p. 392.

[17] E. Jonsson, thesis, Uppsala, 1928 (unpublished). See A. H. Compton and S. K. Allison, Ref. 8, p. 537.

[18] F. B. Malik has also pointed out to us (private communication) that interference terms are missing in the formulations of Stobbe and Hall. The electrons in the L_I shell or the $L_{II,III}$ shell are, in principle, indistinguishable. In the strictest sense, one should work with initial and final wave functions consisting of a Slater determinant of these electrons. This modifies the transition probabilities from L shells to the continuum by adding interference terms that may not be negligible. In fact these interference terms are important in the analogous case of scattering by atoms: I. Waller and D. R. Hartree, Proc. Roy. Soc. (London) **A124**, 119 (1929), W. Heisenberg, Z. Physik **32**, 737 (1931); L. Bewilogua, *ibid.* **32**, 740 (1931).

[19] Alan J. Bearden (private communication, to be published) has calculated photoelectric cross sections for argon, using a modified Stobbe formula. From these calculations we obtain a vacancy distribution for experiment I of L_I, 40%; $L_{II,III}$, 55%; M, 5.5%; and for experiment II: L_I, 48%; $L_{II,III}$, 46%; and M, 5.5%. The observed abundances for Ar^{1+}, Ar^{2+}, and Ar^{3+} (Table I) are in much better agreement with these vacancy distributions than with those obtained from Eqs. (1) and (2).

TABLE III. Relative abundances of ions resulting from vacancies found primarily in the K shell of Ar or ^{37}Cl. Comparison of experiment with theory. Relative abundance, $I(n)$, where $\sum_{n=2}^{n=8} I(n) = 100.0$.

Experiment III. X rays produced from Ti target (cf. Fig. 2, graphs A and B).
Calculation III. Based on the following distribution of vacancies: K shell, 90.2%; L_{I}, 8.0%; $L_{\mathrm{II,III}}$, 1.0%; M, 0.8%.
Experiment IV. X rays produced from Mo target (cf. Fig. 2, graphs C and D).
Calculation IV. Based on the following distributions of vacancies: K shell, 89.1%; L_{I}, 8.9%; $L_{\mathrm{II,III}}$, 0.6%; M, 1.4%.
Experiment V. $Ar^{37} \xrightarrow{EC} Cl^{37}$. For better comparison with x-ray data, the charges are taken as $n+1$.
Calculation V. Based on the following vacancy distribution: K shell, 90.4%; $L_{\mathrm{I}}=9.3\%$; $M=0.3\%$.
A = From Auger processes. B = From Auger processes and electron shake-off.

Charge of ion (n)	Experiment III	Calculation III A	Calculation III B	Experiment IV	Calculation IV A	Calculation IV B	Experiment[a] V	Calculation V A	Calculation V B
1	2.0±1.0	1.6	1.4	···	2.2	2.1	···	1.0	0.9
2	10.6±0.5	12.5	10.7	10.1±1.6	12.1	10.6	6.2±0.1	9.4	9.5
3	13.8±0.5	15.1	14.3	16.4±1.6	16.0	14.5	15.7±0.4	16.4	15.9
4	36.0±0.8	48.6	39.9	33.4±1.6	48.4	40.0	39.2±0.5	49.7	45.8
5	26.4±0.8	18.2	23.0	25.5±2.0	18.0	22.8	26.7±0.4	18.6	20.9
6	10.1±0.7	5.6	9.4	11.1±1.6	5.5	9.4	10.0±0.2	5.9	7.2
7	2.7±0.5	0.0	2.2	3.5±1.1	0.0	2.2	1.8±0.1	0.0	0.6
8	0.4±0.2	0.0	0.5	···	0.0	0.5	0.4±0.1	0.0	0.05

[a] A. H. Snell and F. Pleasonton, Phys. Rev. 100, 1396 (1955).

Electron shake-off occurs when an orbital electron experiences a sudden change in the effective charge. The result is similar whether the change is due to beta decay, or whether it comes from photoelectron emission or from readjustment of the atom by Auger processes. We have estimated electron shake-off by two methods. In one method we have the following relationship, obtained in an earlier paper.[5]

$$P_{nl} \approx (\Delta Z_{\mathrm{eff}})^2 P_{nl}', \tag{3}$$

where P_{nl} is the probability for a shake off of one electron from the nl shell of argon because of the change in effective charge, ΔZ_{eff}; and P_{nl}' is the probability for electron shake-off due to beta decay.

The values of P_{nl}' have been obtained from overlap integrals[20] in conjunction with experimental values[21] from the decay of ^{41}Ar, in a manner described previously[22] for ^{23}Ne. They are $P_{1s}'=0.26\%$; $P_{2s}'=0.91\%$, $P_{2p}'=2.1\%$; $P_{3s}'=4.2\%$; $P_{3p}'=9.6\%$ (another 8.2% of the $3p$ electrons are found in excited states that are still bound).

In the second method, we have calculated the probabilities as first suggested by Migdal[23] from

$$P_{nl}=1-\left|\int \psi_f^* \psi_i d\tau\right|^2, \tag{4}$$

where ψ_i is the initial state for the nl electron with an effective charge Z_{eff}, and ψ_f is the final wave function with an effective charge $Z_{\mathrm{eff}}+\Delta Z_{\mathrm{eff}}$, and the probability for vacating the nl state is P_{nl}. It has been argued that, if the electron vacates its state by electron shake-off, it will probably go into the continuum rather than into an excited state.[22,24] Even if the electron does not reach the continuum, it creates a vacancy that gives rise to autoionization, unless the shake-off has been from the $3p$ shell. In evaluating the case of the $3p$ electrons, we have used the ratio of excited states to continuum states given above for ^{41}Ar. Calculations for electron shake-off have been based on Eq. (3) except for the contributions from photoionization in the L_{I} shell, for which Eq. (4) was used. The latter contributions, however, make up the bulk of the calculated abundances for charges 4 to 6. In the solution of Eq. (4) the initial states were obtained from Hartree-Fock wave functions for the Ar atom, and the final states from Hartree-Fock wave functions of Ar^{1+} with a hole in the $2s$ shell.[25] It was gratifying to find that the probailities using Eq. (4) were in fairly good agreement with the more indirect method using Eq. (3). For example, $\sum_{nl} P_{nl}$ was 10.3% and 10.0%, as calculated, respectively, from Eqs. (3) and (4).

For multiple electron shaking we have employed an expression given earlier,[22] which treats the electron shake-off processes as independent of each other. Our calculations of shaking include all possible changes in the effective charge, the most important being photoelectron emission. Besides direct electron shake-off, consideration is given to excited states which can be involved in autoionization.

The probabilities for losing n electrons are obtained from the products of the probabilities for ionization from Auger processes and from electron shake-off; the resulting charge spectra are listed in columns 3, 5, and 7 of Table II. These results are then combined with the vacancy distribution to arrive at the charge spectra for experiments II and III as computed with consideration of electron shake-off. (Cf. the B columns in Table I.)

[20] T. A. Carlson (unpublished).
[21] T. A. Carlson, Phys. Rev. 131, 676 (1963).
[22] T. A. Carlson, Phys. Rev. 130, 2361 (1963).
[23] A. Migdal, J. Phys. (U.S.S.R.) 4, 449 (1941).
[24] A. E. S. Green, Phys. Rev. 107, 1646 (1957).
[25] These wave functions were computed from a code written by Charlotte Froese.

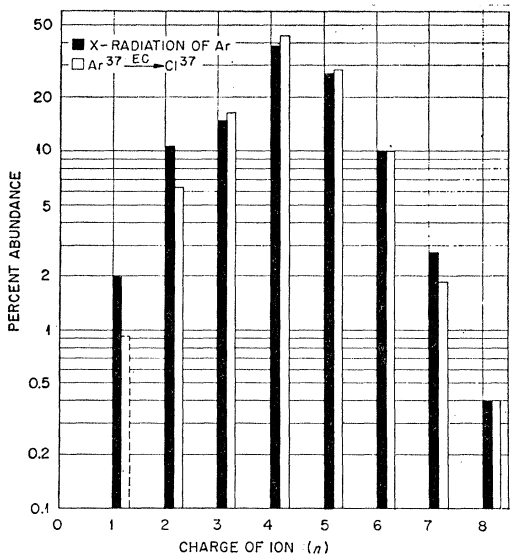

FIG. 4. Comparison of charge spectra resulting from x irradiation of Ar and electron capture in ^{37}Ar. Data for the x-ray studies were taken from experiment III, Table III. Data from the electron capture study were taken from A. H. Snell and F. Pleasonton, Phys. Rev. **100**, 1396 (1955) except for neutral Cl (plotted as charge one), which has been estimated from theory. Data from ^{37}Ar has been adjusted to charge $n+1$.

The additional consideration of electron shake-off has allowed one to explain at least the presence of Ar ions of charges 4 to 6. We note, however, that more ionization has been observed for these ions than can be accounted for. If the vacancy distribution is fitted to match the observed spectrum for the first three charges, this disagreement is even more pronounced. An unaccountably large abundance for the more highly charged ions has already been observed for neon.[5] In both experiments we are forced to the conclusion that either we have grossly underestimated the extent of electron shaking in photoionization, or that there are other processes that have not yet been fully evaluated, such as double x-ray ionization[26] or double electron emission in Auger processes.

B. *K* Vacancies in Ar and ^{37}Cl

The relative abundances of argon ions resulting from the vacancies produced primarily in the K shell are listed in Table III. Data have been taken with two different x-ray sources, whose energy spectra are plotted in Fig. 2. The results of Snell and Pleasonton[3] on the charge spectra of chlorine ions resulting from electron capture of ^{37}Ar are given in column 6. For better comparison of the results, the Cl^{n+} ions are listed as $Cl^{(n+1)+}$, since in electron capture the nuclear charge is lowered by one unit. The relative abundances of ions from charge 2 to 8 have been normalized to 100.0%. The abundances of charge-one ions are given relative to the sum of all the other ions. For a more graphic presentation, the results from experiment III are shown as a histogram, together with the data from electron capture. (Cf. Fig. 4.)

In dealing with the calculated charge spectrum resulting from readjustment to the K shell as opposed to the L shell of argon, we find that the number of possible combinations of radiative and nonradiative transitions have greatly increased. To handle the complex job of evaluating the effect of vacancy cascades, we have made use of a Monte Carlo calculation. The computer picks at random from a table of weighted probabilities one possible transition for filling the initial vacancy. New vacancies introduced by the chosen transition are noted, and the machine selects the next process for filling one of the new vacancies. This continues until no more transitions can be made, and the final number of electrons removed are recorded for this one case. Ten thousand cases were used in generating the charge spectra. We have not attempted to make any changes in the relative transition probabilities as electrons are removed, except to reduce the rate of a given transition proportionally to the number of electrons remaining in the relevant atomic shells. Fortunately, Rubenstein[6] has calculated all the radiative and nonradiative transitions probabilities that are possible for filling vacancies in argon. In fact, an early calculation of the charge spectrum of ^{37}Cl was made by Rubenstein and Snyder[27]

TABLE IV. Transition probabilities for filling electron vacancies in argon.[a]

Initial vacancy	Final vacancies	Transition probability ($e^2/\hbar a_0 \times 10^{-3}$)
$1s$	$2s\ 2s$	1.15
$1s$	$2s\ 2p$	3.74
$1s$	$2s\ 3s$	0.23
$1s$	$2s\ 3p$	0.26
$1s$	$2p\ 2p$	9.38
$1s$	$2p\ 3s$	0.34
$1s$	$2p\ 3p$	1.19
$1s$	$3s\ 3s$	0.01
$1s$	$3s\ 3p$	0.02
$1s$	$3p\ 3p$	0.03
$1s$	$2p$	2.3
$1s$	$3p$	0.173
$2s$	$2p\ 3s$	51.11
$2s$	$2p\ 3p$	63.17
$2s$	$3s\ 3s$	0.62
$2s$	$3s\ 3p$	2.36
$2s$	$3p\ 3p$	0.05
$2s$	$3p$	0.00
$2p$	$3s\ 3s$	0.05
$2p$	$3s\ 3p$	0.90
$2p$	$3p\ 3p$	2.68
$2p$	$3s$	0.00

[a] R. A. Rubenstein, thesis, University of Illinois, 1955 (unpublished).

[26] From measurements of the K absorption spectra of argon, it has been estimated that from 1 to 3% of K photoionization is simultaneously accompanied by M ionization: H. W. Schnopper, Phys. Rev. **131**, 2558 (1963); C. Bonnelle and F. Wuilleumier, Compt. Rend. **256**, 5106 (1963).

[27] R. A. Rubenstein and J. N. Snyder, Phys. Rev. **99**, 189 (1955).

without consideration of electron shake-off. The transition rates are given in Table IV. Note that such transitions as $3s;3p,3p$ are not possible because the difference between the energy of the initial and final states is not large enough to put an electron into the continuum.[13] For the readjustment of chlorine vacancies we have used the same Auger rates as for argon, but have reduced the radiative rates by 20%.[28]

To estimate the effect of electron shake-off for experiments III, IV, and V, we have employed Eqs. (3) and (4) and have followed the general procedures used for experiments I and II as described in Sec. A. The largest contribution to electron shake-off comes from photoelectron emission from the K shell of argon. This case was calculated using Eq. (4) with Hartree-Fock solutions of Ar^{1+} with a $1s$ hole for the final states.[25] Otherwise, calculations were made with Eq. (3). The net change in charge arising from electron capture, and consequently the extent of electron shake-off, is generally small because the reduction in shielding due to the loss of an orbital electron is compensated by the lowering of the nuclear charge. Changes in the effective charge also occur during Auger processes. The amount of electron shake-off due to Auger processes in argon (or chlorine) has been previously calculated by Wolfsberg and Perlman,[29] using hydrogenic wave functions. They found, as we do, that shake-off from the K and L shells due to Auger processes is negligible. They calculated 16% as the probability for vacating the M shell (or 12% using Slater wave functions), as against our value of 11.1%; and they obtained 3% as the probability for transitions to the continuum as against our 6.7%. Wolfsberg and Perlman point out, however, that the relative probability for transitions to the continuum as compared with transitions to excited states is probably too small when calculated with hydrogenic wave functions.

To arrive at vacancy distributions for photoionization in experiments III and IV, we have taken the K/L ratio of 10.0, obtained expermentally at the K edge.[30] This ratio probably holds quite well for experiment III, in which the x-ray energy is close to the edge, though it might not hold so well for experiment IV. The remaining information needed for determining the vacancy distributions was obtained from Eqs. (1) and (2). A small contribution to the initial ionization from Compton scattering was also taken into account.[31] For ^{37}Ar the K/L capture ratio has been measured[32] to be 9.7. The electron capture ratios, $L_{II,III}/L_I$ and L/M were obtained from theoretical tables[33] as 0.002 and 0.034, respectively.

The calculated spectra arising from K vacancies in argon and from K, L, and M vacancies in ^{37}Cl are given in Table V, both with and without consideration of electron shake-off. These spectra and those from Table II are combined with the vacancy distribution to give the calculated charge spectra to be compared with the experimental values for experiments III, IV, and V. (Cf. Table III.)

Good agreement has been obtained between theory and experiment for all three studies listed in Table III. This demonstrates that a vacancy cascade of some complexity can be successfully accounted for, and that Rubenstein's calculations for Auger transitions in argon are fairly reliable.[34] The more complicated spectra of Table III are not ideal cases for checking additional sources of ionization that may supplement the Auger processes; but on examining the abundances of charges 7 and 8, which cannot be explained by Auger processes, we note again that with the exception of charge 8 of experiment III, electron shake-off does not completely account for the observed abundances of the more highly charged ions.[35]

TABLE V. Calculations on the extent of ionization following K vacancies in argon and K, L and M vacancies in ^{37}Cl. (% probability for removing n electrons.)

A = From Auger processes.
B = From Auger processes and electron shake-off.
Calculations on Ar are based on photo-ionization of Ar.
Calculations on ^{37}Cl are based on electron capture of ^{37}Ar.

Total no. of electrons removed (n)	Initial vacancy: K-Ar		K-^{37}Cl		L_I-^{37}Cl		M-^{37}Cl	
	A	B	A	B	A	B	A	B
1	0.9	0.7	0.8	0.7	0.0	0.0	100.0	94.9
2	12.3	10.5	10.1	10.1	2.6	2.6	0.0	5.0
3	7.9	7.8	7.9	7.6	97.4	95.5	0.0	0.1
4	53.0	42.7	54.4	50.2	0.0	1.2	0.0	0.0
5	19.8	25.0	20.4	22.9	0.0	1.4	0.0	0.0
6	6.1	10.3	6.4	7.8	0.0	0.2	0.0	0.0
7	0.0	2.4	0.0	0.65	0.0	0.1	0.0	0.0
8	0.0	0.55	0.0	0.05	0.0	0.0	0.0	0.0

[28] Auger rates are fairly independent of Z, but radiative transitions are dependent on Z^4. For example, see: E. H. S. Burhop, *The Auger Effect* (Cambridge University Press, London, 1952), p. 47.

[29] M. Wolfsberg and M. L. Perlman, Phys. Rev. **99**, 1833 (1955).

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[34] Good agreement with Rubenstein has also been obtained from measurements with an electron spectrometer of the KLL:KLX:KXY Auger electron ratios for argon. P. Erman, J. Rossi, E. C. O. Bonacalza, and J. Miskel, Arkiv. Fysik **26**, 135 (1964).

[35] Values of the relative Auger transitions to the various L subshells may be extrapolated from experimental data as tabulated by W. Mehlhorn and R. G. Albridge, Z. Physik **175**, 506 (1963). The extrapolated values suggest that Rubenstein's calculation may have overemphasized transitions from the L_I shell. If this were true, our calculated values of the more highly charged ions in experiments III, IV, and V would have to be lower, thus emphasizing the discrepancy between theory and experiment for these ions.

CONCLUSION

Atomic readjustment to vacancies in the K and L shells of argon have been studied by measuring the relative abundances of Ar ions formed as the result of such vacancies. For these measurements a new source volume, adapted to the use of x rays, has been used. To interpret the observed charge spectra, calculations have been made of the ions arising from Auger cascades and electron shake-off. Good agreement between theory and experiment has been obtained in studies where vacancies were primarily in the K shell, showing that even for an atomic readjustment of some complexity the main sources for ionization are well understood. We also note, however, particularly with analyses of less complex spectra, viz., those arising from vacancies in the L shell of Ar or the K shells of Ne, that there is more observed ionization than can be presently explained.

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Excitation of the Hydrogen Molecular Ion by Electron Impact

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The cross section for the excitation of the lowest electronic excited state of the hydrogen molecular ion, H_2^+, by electron impact has been computed. The calculation employs the Born approximation and includes exchange effects according to the procedure developed by Bell and Moiseiwitsch. In contrast to the results of a previous calculation, the inclusion of exchange produces only a small increase in the cross section near threshold.

THE excitation of the hydrogen molecular ion by electron impact has been studied by several authors.[1–5] In this process, the ion is excited from the state $1s\sigma_g$ to a higher state, of which the lowest one, $2p\sigma_u$, is the most important. Since the excited state is unstable, dissociation follows excitation.

All but one of the calculations reported to date employ the Born approximation, but only one has included exchange effects.[3,6] In that case, Ivash found that exchange could produce a substantial (order of 10) increase in the total cross section near threshold, and that the results depended very significantly on whether the "post" or the "prior" interaction[7] was employed. By contrast, use of exact rather than approximate wave functions for the molecular ion produces a change in the cross section of only 10% (in the Born approximation without exchange).

Because of the importance of this process in a number of physical situations, we have decided to re-examine the calculation of the excitation cross section in the Born approximation but including exchange. Our work is based on that of Bell and Moiseiwitcsh[8] who derived a general expression for the first-order exchange scattering amplitude free from many of the defects which exist in the usual Born-Oppenheimer approximation.[9] Their result will be discussed in more detail below.

Let $\Psi_0(\mathbf{r})$ be a (one-electron) wave function describing the ground state of the molecular ion, and $\Psi_n(\mathbf{r})$ similarly describe the nth excited state. We are considering the excitation within the framework of the Born approximation so that the incoming electron state is a plane wave (of wave vector $\mathbf{k}_0$); and the outgoing state has wave vector $\mathbf{k}_n$. The Hamiltonian for the two-

[1] E. E. Salpeter, Proc. Phys. Soc. (London) **A63**, 1295 (1950).
[2] E. H. Kerner, Phys. Rev. **92**, 1441 (1953).
[3] E. V. Ivash, Phys. Rev. **112**, 155 (1958).
[4] R. G. Alsmiller ORNL 2766 (1959); ORNL 3232 (1962) (unpublished).
[5] J. Peek, Phys. Rev. **134**, A877 (1964).
[6] The second calculation by Alsmiller cited in Ref. 4 employs the semiclassical Gryzinski method.
[7] H. S. W. Massey in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 36, p. 282. A difference between the "post" and the "prior" results can only occur when approximate wave functions for the molecular ion are used.
[8] K. L. Bell and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A276**, 346 (1963).
[9] We have considered the possible use of Coulomb wave functions instead of plane waves to represent the free electron states. Such wave functions might be expected to yield an improved cross section at the low energies of principal interest here. However, the integrals in Eq. (9) do not appear to be manageable with these functions.