# Electron Shake-Off Resulting from *K*-Shell Ionization in Neon Measured as a Function of Photoelectron Velocity*

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The relative abundances of the differently charged ions that result from photoionization in the *K* shell of neon were measured with a specially designed mass spectrometer. Results were obtained as a function of the x-ray energy from 17.5 to 0.93 keV using characteristic lines from a variety of targets. The charge spectrum resulting from 1.5-keV x rays is as follows: $Ne^{1+}$ 5.7±0.6%, $Ne^{2+}$ 70.2±0.5%, $Ne^{3+}$ 20.8+0.3%, $Ne^{4+}$ 3.0±0.2%, $Ne^{5+}$ 0.28±0.07%. At higher energies the spectrum, with the exception of charge 1, remains essentially the same. At lower energies, however, the relative abundances for ions of charges greater than 2 begin to drop at about 500 eV above the *K* edge of neon. From these data and from previous data on the extent of double electron emission in the *KLL* Auger process, the extent of electron shake-off arising from photoionization has been evaluated. Specifically, it was found that when the photoelectron leaves the *K* shell of neon with a velocity more than $1.5\times10^9$ cm/sec there is a 16% probability for a single electron shake-off, which agrees well with calculations based on the sudden approximation. Simplified calculations on multiple electron ejection were also shown to be in agreement with the observed abundances of the more highly charged ions. Direct collision and electron correlation are discussed as other possible sources for extra electron emission and the data are used to set upper limits to these contributions.

## INTRODUCTION

IONIZATION of an atom as the result of x irradiation arises principally from two sources: (1) the ejection of a photoelectron and (2) Auger processes, which may result from a readjustment to the vacancy created by the photoelectron emission. An Auger process can fill this initial vacancy by having one electron from a higher shell in the atom drop into the hole, while a second goes into the continuum carrying away the excess energy of the transition. The two electrons which have taken part in the initial Auger process leave the atom with two new vacancies. If electrons are available from still higher shells in the atom, these new vacancies may result in additional Auger processes. In a large atom a series of such Auger processes can lead to extensive ionization. In addition to these two principal sources of ionization there are also secondary[1] sources. Such sources are, for example: (1) electron shake-off that accompanies sudden changes in the effective charge, (2) direct collision suffered by photo and Auger electrons as they emerge from the atom, and (3) the phenomenon of electron correlation, which in certain cases is inadequately explained by the present treatment of items (1) and (2). Though they contribute less to the total number of ejected electrons than do the primary sources, these secondary sources can give rise to highly charged ions, otherwise unaccountable, and are germane to the understanding of radiation physics.

Because of its simplicity, a good system for studying the effects of secondary ionization is the photoionization of the *K* shell of neon. A *K* vacancy in neon will lead to a *KLL* Auger process 99% of the time giving $Ne^{2+}$, but will not give rise to any subsequent Auger processes (unless some mode for simultaneous excitation is present). Neon ions of charge higher than two may be therefore attributed to secondary sources of ionization. In an earlier paper[2] we presented data on the relative abundances of ions resulting from x irradiation of neon, which gave evidence for a considerable contribution from secondary sources.

We were able to account for some but not all of this ionization. Meanwhile we have re-examined the problem of *K* photoionization in neon. There are two principal reasons for the re-examination. First, our present spectrometer is free from uncertainties in the relative collection efficiencies that plagued the earlier machine. Second, we have made measurements of the charge spectra of neon as a function of x-ray energy from 17.5 keV to just above the *K* edge of neon. From these measurements we hoped to reveal the source of the additional ionization, previously unexplained.

This hope has been realized. From data that will be given in this paper and from data reported previously, in which secondary ionization accompanying the *KLL* Auger process has been evaluated,[3] we are now able to explain essentially all the ionization observed under conditions where the photoelectron is removed with sufficient velocity so that the sudden approximation is valid. In addition, we shall use our results to evaluate the conditions under which the sudden approximation no longer holds. Finally, we shall discuss two other sources for secondary ionization, viz., direct collision and electron correlation, and shall give probable limits to these contributions.

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[1] In this paper, when we refer to secondary ionization and secondary electrons, we do not use the meanings that are often attached to them in the study of radiation damage. Rather we shall consider the *K* photoionization and the *KLL* Auger processes as primary ionization events, but any additional electrons ejected during photoionization or in the subsequent Auger process will be called secondary electrons.

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

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

TABLE I. X-ray sources used in irradiating neon.

| Type of tube | $E_{max}$[c] | Target | Filter (mg/cm²) | $E_{line}$[d] |
|---|---|---|---|---|
| $A$[a] | 52 | Mo | 230 Be+52 Mo+34 Al | $K_\alpha$ 17.5 |
| $A$ | 41 | W | 56 Be+27 Al | $L_\alpha$ 8.4 |
| $A$ | 20 | Ti | 47 Be+11 Ti | $K_\alpha$ 4.5 |
| $B$[b] | 6.5 | Al | 4.7 Al | $K_\alpha$ 1.49 |
| $B$ | 4.0 | Mg | 1.4 Al | $K_\alpha$ 1.256 |
| $B$ | 4.0 | Zn | 0.70 Zn+0.11 polystyrene | $K_\alpha$ 1.014 |
| $B$ | 4.0 | Cu | 0.45 Cu+0.11 polystyrene | $L_\alpha$ 0.932 |

[a] Machlett AEG–50.
[b] Designed by J. A. Bearden: Cf. Ref. 4 for further description.
[c] Maximum energy in keV of electrons striking the target.
[d] Designation and energy in keV of the most prominent characteristic line.

## EXPERIMENT

In brief, our experiment consisted of measuring the relative abundances of the differently charged neon ions that result from x-ray bombardment. To accomplish this, we allowed neon to leak into a chamber of a specially designed mass spectrometer, where the gas was irradiated. Ions formed in the source volume were extracted and magnetically analyzed. The experimental procedures and equipment have been described in some detail in a previous paper[4] on Ar. The reader is reminded, however, that gas pressures in our experiments are kept sufficiently low to preclude alterations of the charge spectra due to ion-molecule reactions, and that the time for collecting the ions, about $10^{-6}$ sec, is very long compared to the time needed for the various self-ionization processes under investigation to take place, less than about $10^{-14}$ sec. Studies parallel to those reported for Ar that are related to the assessment of possible experimental errors, such as those that arise from high pressure and differences in collection efficiencies, were also carried out on neon.

In the present experiment a variety of x-ray sources were used, which are listed in Table I. Further details on the two different types of x-ray tubes and their operating conditions can be found in our earlier publication.[4] For each source of x rays the filters strongly favor the transmission of a $K_\alpha$ or $L_\alpha$ characteristic line, and thus for each run we have taken this line to be the primary source for producing vacancies in the $K$ shell of neon. The correctness of this assumption has been demonstrated by measurements of the x-ray spectra for the Mo and Ti targets.[5] We have also assessed the contribution of bremsstrahlung in the runs with Mg, Zn, and Cu targets since the charge spectrum of neon was fairly sensitive to the energy of the x rays for these three runs. (One might also be concerned with the $L_\beta$ line in Zn and Cu, but these lines are strongly absorbed in the targets and by the filters.) For each of these three runs we have made a background measurement, in which the charge spectrum was measured using a V target with the same filters and applied voltages. Since no characteristic lines of V are present between the applied voltage, 4 keV, and the $K$ edge of neon, one may use the data from such a target to estimate the amount of bremsstrahlung plus any possible contamination to the target from the tungsten filament. (Tungsten contamination of the target was also checked in each run by examining, immediately after the installation of a fresh target, the charge spectrum as a function of time.) The "backgrounds" derived from the V target showed that only about 5% of the vacancies in the case of the Zn run and 20% in the case of the Cu and Mg runs were due to x rays other than the characteristic lines. The results of the V runs were subtracted from the charge spectrum of the corresponding runs with the last three targets. The errors quoted for the corrected relative abundances are increased so as to equal the magnitude of these corrections. Only in the case of the measurement of $Ne^{4+}$, using the Cu target, were the data very sensitive to these corrections.

[4] T. A. Carlson and M. O. Krause, Phys. Rev. **137**, A1655 (1965).
[5] Cf. Ref. 4, Fig. 2.

## RESULTS AND DISCUSSION

In Table II we have given the charge spectrum of neon as a function of the energy of the incident x rays. Singly charged neon is essentially a measurement of the amount of $L$ ionization, since about 99% of the $K$ vacancies result in multiply charged ions,[6] while most of the time, 87%,[7] $L$ vacancies give $Ne^{1+}$. Using these respective contributions to charge 1 from the $K$- and $L$-shell vacancies, and the relative $K/L$ cross sections as estimated from the $K$ jump in neon,[8] we calculate that the percent abundance of $Ne^{1+}$ should be about 6.5, which is in good agreement with the data in Table II. In runs using the molybdenum and tungsten $L$ lines contributions from ionization by stray electrons made measurements on $Ne^{1+}$ unreliable. Thus, for these two runs we have estimated $Ne^{1+}$ to be 6.5% plus a contribution from Compton scattering,[9] which is no longer negligible above 5 keV.

In column 6 of Table II we have listed data taken previously[2] with a spectrometer of a different design. With this spectrometer coincidences between the ion and the ejected electrons were measured, which caused the determination of the relative abundances of the

[6] As obtained from $100(1-\omega)$, where $\omega$ is the fluorescence yield in neon. Measurements of the fluorescence yields for low $Z$ are accompanied by rather large uncertainties. Recent experimental values for neon give 0.018, J. Heintz, Z. Physik **143**, 153 (1955); and 0.043, W. F. Frey, R. E. Johnston, and J. I. Hopkins, Phys. Rev. **113**, 1057 (1959). A semiempirical evaluation by H. L. Hagedorn and A. H. Wapstra, Nucl. Phys. **15**, 146 (1960) gives 0.006. From the evaluation of our data on $Ne^{1+}$ we would seem to favor about 0.01.
[7] The charge spectra obtained for neon from x rays of energies just below the $K$ edge has been measured as: $Ne^{1+}$, 87%; $Ne^{2+}$, 12%; and $Ne^{3+}$, 1%: T. A. Carlson (to be published).
[8] As obtained from absorption data given by J. A. Victoreen, J. Appl. Phys. **20**, 1141 (1949). (Strictly speaking, the $K/L$ ratio probably rises slightly with increasing x-ray energy.)
[9] E. Storm, E. Gilbert, and H. Israel, Office of Technical Services, Washington, D. C., Report No. LA-2237, 1958 (unpublished).

TABLE II. Charge spectra of neon resulting from photoionization in % abundance. (Values in parentheses are estimates.)

| Ion \ $E$[a] | 0.932 | 1.014 | 1.256 | 1.5 | 1.5[b] | 4.5 | 8.4 | 17.5 |
|---|---|---|---|---|---|---|---|---|
| $Ne^{1+}$ | 7.0 ±0.7 | 6.8 ±0.7 | 6.5±0.7 | 5.7 ±0.6 | 3 | 8 ±2 | (7) | (13) |
| $Ne^{2+}$ | 82.9 ±1.3 | 74.2 ±1.2 | 68.5±2.0 | 70.2 ±0.5 | 66 | 69 ±2 | 70 ±2 | 63±5 |
| $Ne^{3+}$ | 9.9 ±1.2 | 17.6 ±0.6 | 22 ±2 | 20.8 ±0.3 | 24 | 19.5±2 | 20.4±0.8 | 20±3 |
| $Ne^{4+}$ | 0.2 ±0.2 | 1.3 ±0.2 | 2.8±0.5 | 3.0 ±0.2 | 6 | 3.5±0.8 | 2.7±0.4 | 4±3 |
| $Ne^{5+}$ | <0.04 | 0.08±0.04 | (0.3) | 0.28±0.07 | 0.8 | (0.3) | (0.3) | (0.3) |

[a] Energy of x rays in keV.
[b] M. O. Krause, M. L. Vestal, W. H. Johnston, and T. A. Carlson, Phys. Rev. 133, A385 (1964).

differently charged ions to be dependent on the collection efficiencies for the electrons. An attempt was made in that study to remove the uncertainty by rejecting electrons of energies of less than 100 eV, since it was felt secondary[1] electrons had energies less than this amount. Thus, regardless of the extent of secondary ionization, only two electrons, the photoelectron and the *KLL* Auger electron, should have been collected (except for $Ne^{1+}$ in which only the photoelectron is present). The large relative abundance of the more highly charged ions as indicated by the data in column six suggests the assumption is not entirely correct; i.e., some of the secondary electrons, apparently do have considerable energy. A study of the energy distribution of these secondary electrons should be of great interest, and we plan to carry out such measurements in the future.

Since we are primarily concerned with the results arising from $K$ ionization, we have corrected the data in Table II for contributions from $L$-shell photoionization. This has been done in each study by subtracting 1% (the contribution of a $K$-shell vacancy that is filled by a radiative transition) from the relative abundance of $Ne^{1+}$, which should give the approximate amount of $Ne^{1+}$ resulting from $L$-shell photoionization. The contribution to the ions of charge greater than one can then be obtained with the help of the charge spectrum for $L$-shell photoionization in neon measured in a previous experiment.[7] In every case the corrections to the multiply charged ions were negligible. We then normalized to 100% the relative abundances for ions of charge two and above. The data, which are given in Table III, can be thought of in terms of the probability for secondary emission.[1] The ions $Ne^{2+}$, $Ne^{3+}$, $Ne^{4+}$, and $Ne^{5+}$ represent, respectively, the emission of zero, one, two, or three secondary electrons. We have also included in Table III results reported earlier,[3] in which the charge spectrum was measured with x rays whose energies were insufficient to simultaneously cause ionization in both the $K$ and $L$ shells. (The secondary ionization that is observed arises solely from the action of the *KLL* Auger process.)[10] The data from Table III have also been plotted in Fig. 1 against the energy of the photoelectron (i.e., the x-ray energy minus the binding energy for the $K$ shell of neon, 867 eV). For photoelectron energies above about 500 eV, the amount of secondary electron emission is fairly constant, but below this value it begins to decrease, though not to zero. The energy limits for secondary ionization have also been indicated in Fig. 1. Below these limits the x ray does not possess sufficient energy to cause the ionization of $n$ secondary electrons.[11] (See, however, Ref. 12 for a discussion of the role of excited states in ionization.) For observations made below these limits, at least one of the secondary electrons must have been ejected during the subsequent *KLL* Auger process. The data obtained for energies just above the $K$ edge, Table III, column 2, are shown by dotted lines. Note the limit for double $K$ emission. Since such an event would lead principally to $Ne^{4+}$ (2 vacancies, each accompanied by an Auger process), the absence of any increase in the abundance of the charge-4 ion above the energy limit for double $K$ emission indicates that this event occurs with less than about $\frac{1}{2}$% probability, the approximate error in the difference between the abundance of $Ne^{4+}$ at 670 eV and those taken above 1010 eV. This result may be compared with about 4% double $K$ photoelectron emission measured for He.[13] This de-

[10] The *KLL* Auger process in neon has about 800 eV excess energy available, which the primary electron normally takes up in the form of kinetic energy. It also occurs, however, that part of the energy can sometimes be transferred to a secondary electron. Incidentally, it should be possible to separate the effects of photoelectron emission from the subsequent Auger process, since the half-life of the Auger process, about $10^{-15}$ sec, offers sufficient time to remove the photoelectron completely from the atom and for the remaining atomic electrons to reach at least quasistationary states.

[11] These are the energies necessary to remove one or more electrons from $Ne^{1+}$ having the configuration $1s$, $2s^2$, $2p^6$. The first three energy limits are for the removal of $n$ electrons from the $2p$ shell; the highest limit is for the removal of the $1s$ electron. The values have been obtained from Hartree-Fock solutions and from the interpolation of the ionization potentials of the various charge states of sodium and neon with the help of Slater's rules for screening constants. For more details see footnote 7 of Ref. 3.

[12] Excited states of relatively long half-lives could be formed as the result of photoionization, which might in some cases lead to additional ionization when the Auger process occurs. The energy limits for such states would probably lie about 10, 25, and 60 eV below the respective ionization limits, given in Fig. 1, for one, two, and three secondary electrons as suggested by the atomic energy levels for the various charge states of Ne and Na ions: C. E. Moore, Natl. Bur. Std. (U. S.) Circ. **467** (1949). We believe that such excited states play only a minor role in secondary ionization. In any case, the data that was obtained on secondary ionization due solely to the *KLL* Auger process (cf. Ref. 3) are essentially free from contributions of these excited states.

[13] T. A. Carlson (to be published). See also T. A. Carlson and M. O. Krause, Bull. Am. Phys. Soc. **10**, 455 (1965).

TABLE III. Probability (%) for secondary electron[a] emission as the result of photoionization in the $K$ shell of neon. (Values in parentheses are estimates.)

| No. of secondary electrons $E_e$[b] | 0–0.046[c] | 0.065 | 0.147 | 0.389 | 0.62 | 3.6 | 7.5 | 16.6 |
|---|---|---|---|---|---|---|---|---|
| 0 | 92.1 | 89.1 | 79.5 | 73.1 | 74.4 | 74.5 | 74.6 | 72 |
| 1 | 7.5±1.0 | 10.6 ±1.4 | 19.0 ±0.6 | 23.6±2.2 | 22.1 ±0.3 | 21.4±1.9 | 22.1±0.8 | 24±4 |
| 2 | 0.4±0.2 | 0.3±0.3 | 1.4 ±0.2 | 3.0±0.5 | 3.2 ±0.1 | 3.8±0.8 | 3.0±0.4 | 4±3 |
| 3 | (0.0) | 0.05 | 0.09±0.05 | (0.3) | 0.30±0.08 | (0.3) | (0.3) | (0.3) |

[a] Cf. Ref. 1 for definition.
[b] Energy of the photoelectron in keV.
[c] T. A. Carlson and M. O. Krause, Phys. Rev. Letters **14**, 390 (1965).

crease of secondary ionization for a given shell with an increase in $Z$ is reasonable, since electron shake-off decreases[14–17] as $1/Z^2$, and it is suspected[18] that the over-all effect that electron correlation has on secondary ionization also decreases as $1/Z^2$.

## ELECTRON SHAKE-OFF AND THE SUDDEN APPROXIMATION

### A. The Sudden Approximation

Let us consider a system that has been left to itself for a long time so that it has settled down to some stationary state. Let this system then undergo a sudden change in the Hamiltonian. Since the wave function must remain continuous during this abrupt change, the new wave function describing the system can be shown[19] to be composed of overlap integrals between the wave functions for the original state and solutions for the various possible final states. Thus the probability for finding an electron originally in the state designated by the wave function $\psi_i$ to be in a final state $\psi_f$ is given by

$$P_{i\to f}=\int\left|\psi_f{}^*\psi_i d\tau\right|^2. \qquad (1)$$

The change in the wave function during the time $t$ when the Hamiltonian is being transformed is of the order of $e^{i(\epsilon_i-\epsilon_f)t/\hbar}$, where $\epsilon_i$ and $\epsilon_f$ are the energy levels involved in the transition under discussion. The criteria for the sudden approximation is that

$$(\epsilon_i-\epsilon_f)t/\hbar\ll 1. \qquad (2)$$

In our experiment a change in the Hamiltonian arises as the result of $K$ photoionization because of the alteration in electron shielding. When the change is sudden, there is a possibility that an electron experiencing the difference in the effective charge may find itself in the continuum. This phenomena is known as electron shake-off, and results obtained with the removal of a photoelectron are closely akin to those observed in beta decay.[20]

Let us consider the electron shake-off of an outer electron in neon due to $K$ photoionization. The energy of the electron in the initial state is the ionization potential for neon $I$, while in the final state it is the energy of the free electron. Since an electron is usually removed in shake-off with only a small amount of kinetic energy,[16] we have set $\epsilon_f=0$. To find an approxi-

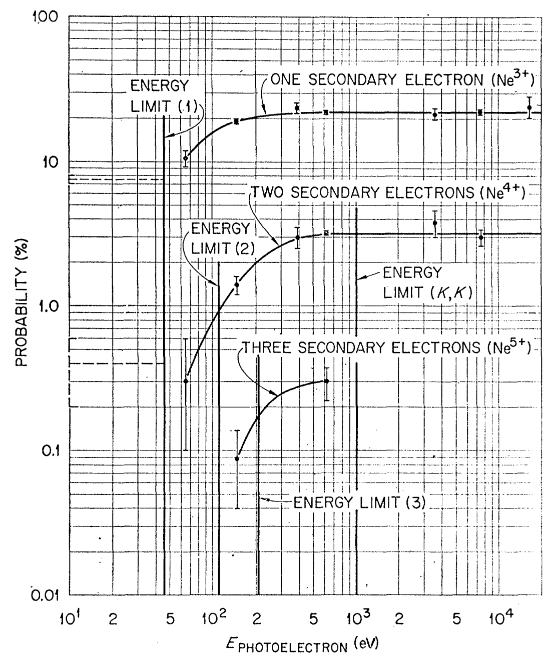


FIG. 1. Probability for secondary electron emission (cf. Ref. 1 for definition) as the result of photoionization in the $K$ shell of neon. The % probability for one, two, and three secondary electrons are taken from the experimentally determined relative abundances of $Ne^{3+}$, $Ne^{4+}$, and $Ne^{5+}$ where $\Sigma_{n=2}{}^{n=5}\,Ne^{n+}=100\%$. The energy limits ($n$) are the threshold energies necessary for removing $n$ electrons from $Ne^{2+}$ having the configuration $1s$, $2s^2$, $2p^6$. The energy limit $(K,K)$ is that necessary to remove both $K$ electrons. The dotted lines give the contribution to secondary electron emission due solely to the $KLL$ Auger process.

[14] E. L. Feinberg, J. Phys. (USSR) **4**, 423 (1941).
[15] A. Migdal, J. Phys. (USSR) **4**, 449 (1941).
[16] J. S. Levinger, Phys. Rev. **90**, 11 (1953).
[17] H. M. Schwartz, J. Chem. Phys. **21**, 45 (1953).
[18] T. A. Welton (private communication).
[19] For a discussion of the sudden approximation, cf. D. Bohm, *Quantum Theory* (Prentice-Hall, Inc., New York, 1951), pp. 507–509.
[20] For calculations of electron shake-off in beta decay, see Refs. 14–17. For discussions relating electron shake-off in photoionization to that in beta decay, see Refs. 2 and 4.

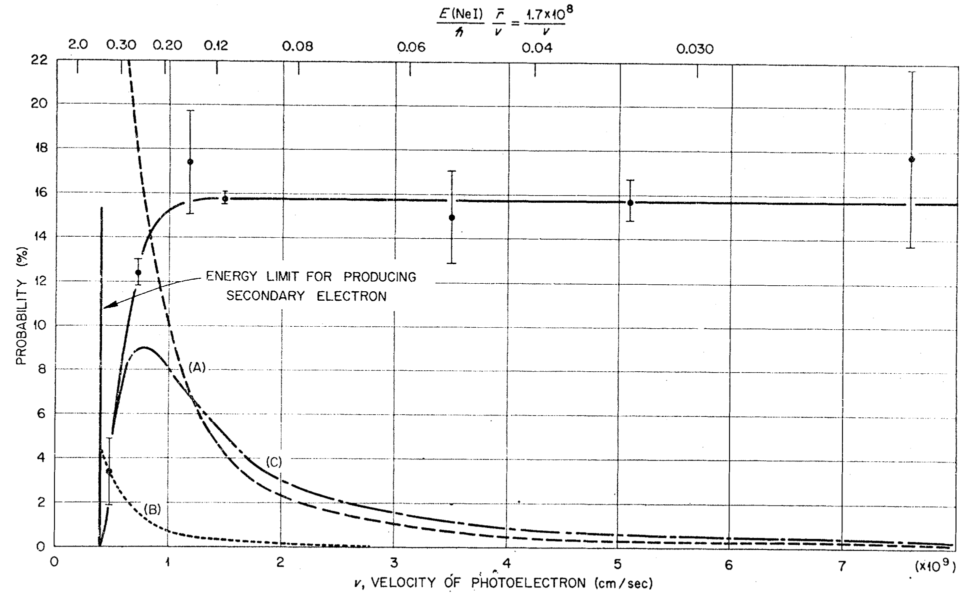


FIG. 2. Dependence of electron shake-off, resulting from photoionization in the $K$ shell of neon, on the velocity of the photoelectron. Data have been obtained from Eq. (5) and represent the probability that one secondary electron (cf. Ref. 1 for definition) will be ejected solely as the result of energy available in photoionization. The upper scale relates the data to the sudden approximation since $(1.7/v)\times10^8\approx[(\epsilon_m-\epsilon_n)/\hbar]t$ [cf. Eq. (4)]. A solid line is fitted to the data. Curve (A) gives the values for direct collision as calculated from Eq. (6). (B) and (C) represent possible velocity dependence for direct collision made to pass through the data at $v=0.48\times10^9$ cm/sec. (B) is dependent on $v^{-2}$ and (C) has a shape derived from electron impact studies (cf. Ref. 24).

mate value for $t$, we have used the time to remove an electron from the neon atom, as given by

$$t\approx\bar{r}/v, \tag{3}$$

where $\bar{r}$ is the mean radius of the $2p$ shell of neon and $v$ is the velocity of the photoelectron in cm/sec. Therefore,

$$\frac{(\epsilon_i-\epsilon_f)t}{\hbar}\approx\frac{I\bar{r}}{\hbar v}=\frac{1.7\times10^8}{v}. \tag{4}$$

In Fig. 2 the probability for the shake-off of one electron has been plotted against the velocity of the photoelectron. We have also displayed at the top of the graph the values from Eq. (4), so as to ascertain the magnitude of $[(\epsilon_i-\epsilon_f)/\hbar]t$ at the point where the sudden approximation breaks down. The probabilities for electron shake-off are taken from the experimental data on the relative abundance of $Ne^{3+}$. However, since the data includes not only contributions to secondary ionization that arise directly because of the photoionization, but also a contribution from the double electron emission that may occur in the $KLL$ Auger process,[3] this latter contribution must be subtracted. This is done by means of the relation

$$x=\frac{y-a}{1-a/100}=\frac{y(E)-7.5}{0.925}, \tag{5}$$

where $x$ is the percent probability for the ejection of a secondary electron from the $L$ shell due to $K$ photoionization, $y$ is the percent abundance of $Ne^{3+}$ from Table III as a function of energy, and $a$ is the percent abundance for ejection of a secondary electron due only to the $KLL$ Auger process and is essentially independent of the photoelectron energy.[21]

Before we can evaluate the significance of Fig. 2 solely in terms of *electron shake-off*, we need to discuss two other possible sources of secondary ionization. They are *direct collision* and *electron correlation.*

### B. Direct Collision

Let us consider the possibility for a direct collision between the emerging photoelectron and one of the $L$-shell electrons of the same atom. Feinberg has examined the relative roles of direct collision and electron shake-off in beta decay. His earlier[14] conclusion was that direct collision is negligible. Recently,[22] he has suggested that this may not always be true. The probability that a $\beta^-$ particle will collide with an electron in the $L$ shell is closely related to our problem, since the $\beta^-$ particle emerges from the center of the atom, while an electron ejected from the $K$ shell emerges from near the center. (In neon the mean radius for the $K$ shell is about $\frac{1}{6}$ that of the $L$ shell.) Feinberg[22] gives

$$W_{\text{dc}}=\alpha^2[2E^2/(E^2-1)]Q, \tag{6}$$

where $W_{\text{dc}}$ is the probability that the $\beta^-$ particle will make a direct collision with one of the atomic electrons, $\alpha$ is the fine structure constant, $E$ is the energy of the $\beta^-$ particle in mc² units, and

$$Q=\int_0^\infty f(Z,\epsilon_{\text{min}},\phi(\chi))d\chi, \tag{7}$$

where $Z$ is the number of electrons in the atom, $\epsilon_{\text{min}}$ is the arbitrarily chosen minimum for the energy of the

[21] There could be some change in the probability for secondary ionization that accompanies the Auger process, if multiple photoionization has taken place, but this is a second-order effect. As to the possibility of interaction between excited states that might result from photoionization and the subsequent Auger process, cf. Ref. 12.

[22] E. L. Feinberg, *On the Ionization of the Atom Due to Beta Decay* (Academy of Sciences of the USSR, Moscow, 1964).

electron which is ejected following the direct collision with the $\beta^-$ particle, and $\phi(\chi)$ is the tabulated Thomas-Fermi function. In order to evaluate $Q$ so that it could be applied to our problem, two assumptions were necessary. (1) We have given $\epsilon_{\min}$ the value of 1 Ry. If $\epsilon_{\min}$ is set equal to zero, the expression for $Q$ [Eq. (26) in Ref. 22] blows up. In fact, Feinberg's treatment of direct collision is only approximate when $\epsilon_{\min} \lesssim I$, where $I$ is the ionization potential of the electron that is ejected following the collision. By choosing $\epsilon_{\min}$ to be 1 Ry, we should have a value sufficiently low in energy to include most of the knocked-out electrons while at the same time not so low as to strain the validity of the formula. Fortunately, $Q$ is rather insensitive to the choice of $\epsilon_{\min}$. The error arising from this choice should not alter $Q$ more than a factor of 2.[23] (2) Rather than carry out the integration of $Q$ down to $\chi=0$, we have chosen the value suggested by Feinberg of $\chi \approx Z^{-2}$. With this value one avoids the uncertainty of the Thomas-Fermi method at small atomic radii, and also avoids including the contribution of direct collision with the $K$ electrons. With these two assumptions we have calculated that in the case of neon $Q \approx 1$. By setting $Q$ equal to 1 in Eq. (6) we have the formula for direct collision that we were seeking. The results as a function of the velocity of the photoelectron are given in Fig. 2. For photoelectrons whose energies are considerably above the ionization threshold, the calculations on direct collision are not inconsistent with the data; but at energies just above the threshold, the calculated values are far in excess of the total ionization measured experimentally. However, Feinberg's treatment of direct collision has been based on cases where $E \gg 1$ and thus cannot be expected to hold near the threshold.

If we examine in Fig. 2 the point taken at $v=0.48 \times 10^9$ cm/sec, we note that there is still about a 3% probability for secondary electron ejection due to $K$ photoelectron emission. Let us use this value to set an upper limit for direct collision by assuming that all the ionization at this point is due to direct collision. According to Feinberg, $W_{dc}$ is approximately dependent on $v^{-2}$ and this dependence is plotted in Fig. 2. However, one might also expect to find a maximum in the $W_{dc}$ curve, such as found with electron-impact studies. Thus, in Fig. 2 the dependence of $W_{dc}$ on the photoelectron velocity is also plotted having a shape suggested by electron-impact data.[24] A comparison of direct collision from electrons originating from outside the atom and from those ejected from the inside must be viewed with caution, particularly with regard to the initial rise of the cross section with electron energy.[25] In electron impact this initial rise may be qualitatively described[26] as follows: The atom receives both head-on and glancing impacts. The latter are capable of only partial energy transfer. Thus, as the energy of the electron increases, more and more of the glancing impacts can result in ionization; and the cross section rises. From the geometrical nature of the two processes, one might expect to find more glancing impacts from a flux of electrons striking the atom from the outside, than from the emergence of an electron from the inside of the atom.

A better theory is certainly needed for direct collision in photoelectron emission.

### C. Electron Correlation

Recent studies[7,13] have been made on photoionization in the outermost shells of He, Ne, and Ar, in which considerable multiple ionization has been observed. As with electron shake-off, the amount of secondary ionization was fairly constant with increasing photoelectron energy, at least for values several times above the energy at the ionization threshold. However, calculations of electron shake-off could account for only a third of the observed secondary ionization. It is presently thought that the source of this excess ionization might be explained, if the photoionization process could be described as a many-body problem,[27] which explicitly includes electron correlation. (It is also believed that the observed double electron ejection from the valence shells of neon,[3] argon,[13] and krypton[28] as the result of Auger processes, i.e., the $KLLL$ transition in Ne, the $LMMM$ transition in Ar, and the $MNNN$ transition in Kr, are likewise related to the problem of electron correlation.[27]) Salpeter and Zaidi,[29] using a two-electron Hylleras-type wave function for the ground state of He, calculated the probability for simultaneous excitation of one electron to the 2$s$ state of He, while the other was undergoing photoionization. This calculation gave

[23] For example, when $\epsilon_{\min}$ was set at $\frac{1}{10}$ Ry, $Q$ rose to 1.7 of its value at 1 Ry, while when $\epsilon_{\min}$ was put equal to $I$ (46 eV), $Q$ dropped to 0.6.

[24] This shape is taken by plotting experimental data on the relative cross section for forming $Ne^{1+}$ by electron impact as a function of the energy of the bombarding electrons in excess of the ionization potential: P. T. Smith, Phys. Rev. **36**, 1293 (1930); W. Bleakney, *ibid.* **36**, 1303 (1930).

[25] Williams showed that electron impact is composed of two parts, one related to the direct collision of two bodies and the other arising from the "photo effect" on the whole atom, E. J. Williams, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. **13**, No. 4 (1935). T. A. Welton pointed out to us in a private communication that when an electron emerges from the center of the atom, direct collision is given by the first part, while the "photo effect" is already contained in the description given by electron shake-off.

[26] Cf., for example, F. H. Field and J. L. Franklin, *Electron Impact Phenomena* (Academic Press Inc., New York, 1957), p. 53.

[27] Note that describing initial and final states as many-electron-wave functions in the form of antisymmetrized sums of products of orthogonalized single-electron states means that a perturbing energy in the form of a one-particle operator (photoionization) can eject only one electron. Similarly, a perturbing energy in the form of a two-electron operator (Coulomb interaction) may involve only two electrons, of which one is in the continuum in the case of an Auger process. With real functions we expect departures from these rules of the magnitude determined by the electron correlation present in the actual states.

[28] M. O. Krause and T. A. Carlson (to be published). See also T. A. Carlson and M. O. Krause, Bull. Am. Phys. Soc. **10**, 549 (1965).

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

a value more than twice that calculated from electron shake-off using Eq. (1). It might be anticipated that the same discrepancy would occur if a many-body calculation were made of both electrons going to the continuum. As will be shown in the next Section, electron shake-off calculations for the present experiment are in good agreement with the observed amount of secondary ionization that accompanies the photoelectron emission. That is, in the case of $K$ photoionization in neon the sudden approximation seems to offer a satisfactory description of the secondary ionization, and it does not seem necessary to explicitly account for the effect of electron correlation by means of a many-body calculation. It may be that the problem of properly accounting for electron correlation is most difficult when one deals with the outermost shells, where the effective charge is lowest, and both the primary and secondary ejected electrons emerge from the same shell.

### D. Electron Shake-Off

Though there remains some uncertainty in the roles played by electron correlation and direct collision, it should be permissible to describe from Fig. 2 the dependence of electron shake-off on the photoelectron velocity as follows: The probability for electron shake-off as the result of photoionization is independent of the velocity of the photoelectron until $(\epsilon_i-\epsilon_f)t/\hbar$ is less than about 0.2, but below this value it decreases rapidly. Since the amount of electron shake-off drops sharply just before the ionization potential and seems to be headed toward zero before it reaches this energy limit, the relationship between the ionization potential and electron shake-off is probably more explicit than Eq. (4) would suggest. That is, aside from the breakdown in suddenness, there also may be specific problems just above the ionization threshold related to a mechanism for having the photoelectron transfer nearly all its energy to the shake-off process.

Let us now turn our attention to the region where the sudden approximation is valid in order to see whether the observed ionization can be successfully calculated in terms of electron shake-off. Our first calculation is based on an evaluation of the probability for any electron to vacate its shell $nl$, where $n$ and $l$ are, respectively, the principal and angular momentum quantum numbers, and $N$ is the number of electrons in the shell. The probability is given by[30]

$$P_{nl}=\left[1-\left|\int\psi_{f,nl}{}^*\psi_{i,nl}d\tau\right|^2\right]^N, \tag{8}$$

where $\psi_{i,nl}$ and $\psi_{f,nl}$ are Hartree-Fock solutions of single-electron wave functions for the initial and final states as the result of $K$ photoionization in neon.[31] The probabilities of vacating the $1s$, $2s$, and $2p$ shells are, respectively, 0.06%, 1.9%, and 16.2%. Ignoring the contribution of $P_{1s}$, which will result in an extra Auger transition, we give the calculated probability (theory I) that one and only one electron will undergo electron shake-off due to $K$ photoionization as

$$P_{\rm I}=\sum_{nl}P_{nl}-M=15.1\%, \tag{9}$$

where $M$ is a correction for multiple-electron shake-off as estimated from Eq. (6) of Ref. 30c. If a $2p$ electron vacates its shell, it may be in an excited but bound state, although comparisons between experiment and theory in $\beta^-$ decay suggest that most of the $2p$ vacancies will result in transitions to the continuum.[30c]

Alternatively, the extent of electron shake-off can be estimated semiempirically (theory II) by the following expression

$$P_{\rm II}=\left(\frac{\sum_{nl}P_{nl}-M}{\sum_{nl}P_{nl}'-M'}\right)P'=15.2\%, \tag{10}$$

where $P_{\rm II}$ is the probability for single-electron shake-off due to $K$ photoionization in neon, $\sum_{nl}P_{nl}'-M'$ is calculated in an analogous fashion to Eq. (9) for the case of electron shake-off in the $\beta^-$ decay of $Ne^{23}$, and $P'$ is the experimentally determined[30c] amount of single-electron shake-off in the beta decay of $Ne^{23}$. Note that theory II underestimates the extent of ionization, since it does not take account of a possible interaction between an excited state that might form in the initial photoionization and a subsequent Auger process.[12] Thus, theory II omits consideration of excited states that might result in ionization, while theory I includes contributions from excited states that may not result in ionization. The fact that both theory I and II give about the same result suggests that such excited states do not play a very important role.

A comparison of the calculations given above is made with experiment in Table IV, where the experimental

TABLE IV. Probability (%) for single-electron shake-off following photoionization in the $K$ shell of Ne.

| Theory I[a] | Theory II[b] | Experiment |
|---|---|---|
| 15.1 | 15.2 | 15.8 |

[a] Calculations based on overlap integrals.
[b] Semiempirical calculation based on electron shake-off following the $\beta^-$ decay of $Ne^{23}$.

[30] For this manner of treating the electron shake-off problem, see, for example, (a) A. Winther, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. **27**, No. 2 (1952), (b) A. E. S. Green, Phys. Rev. **107**, 1646 (1957), and (c) T. A. Carlson, *ibid.* **130**, 2361 (1962).

[31] The initial state is the neon atom and the final state is $Ne^{1+}$ with the configuration $1s$, $2s^2$, $2p^6$. The solutions have been computed on a Control Data 1604-A from a program most generously supplied to us by Charlotte Froese of the University of British Columbia. Substantially identical results were obtained using corresponding self-consistent-field state wave functions given by P. S. Bagus, Phys. Rev. **139**, A619 (1965).

TABLE V. Probability (%) for multiple secondary electron[a] ejection following photoionization of the $K$ shell of neon, as determined under conditions where the sudden approximation is valid.

| No. of secondary electrons ejected | Theory $S_n$ | $A_{n'}$ | $P_{n+n'}$ | Total | Experiment |
|---|---|---|---|---|---|
| 1 | 15.1 | 7.5 | −2.4 | 20.2 | 22.0 |
| 2 | 1.4 | 0.4 | 0.9 | 2.7 | 3.2 |
| 3 | 0.1 | 0.0 | 0.2 | 0.3 | 0.3 |

[a] Cf. Ref. 1 for definition.

value is taken from Fig. 2 at high photoelectron velocity. The agreement between theory and experiment is good and it appears that electron shake-off as the result of ionization can be satisfactorily accounted for under conditions where the sudden approximation is valid.

### E. Multiple Secondary Ionization

Evidence of single, double, and triple secondary ionization in our experiment is given by the relative abundance of $Ne^{3+}$, $Ne^{4+}$, and $Ne^{5+}$. From Fig. 1 we see that all three ions have the same general dependence on energy, although at lower energies, when the percent abundances of these ions begin to drop, the decrease is more rapid for the more highly charged ions. This can be partially understood by the assumption that double- and triple-electron shake-off would depend on the second and third power of the probability for single-electron shake-off, and partially on the fact that the ionization thresholds for removing two and three $L$ electrons are higher.

One of the main concerns in our previous investigation[2] on neon was the large discrepancy between experiment and calculations for the more highly charged ions. Part of the disagreement has been removed with more reliable experimental results, but there was at that time also a lack of knowledge as to the role played by the Auger process in giving rise to secondary ionization. We are now in a good position to re-estimate the abundance of $Ne^{4+}$ and $Ne^{5+}$ expected from photoionization in the region where the sudden approximation is valid. First, we have calculated the probabilities for single-, double-, and triple-electron shake-off by putting the values for shake-off given in the previous section into an expression derived earlier[30c] for multiple-electron shake-off. Next, we considered the contributions from the Auger process. Single and double secondary electron emission in the Auger process have been measured[3] to be 7.5 and 0.4%. In addition, we have estimated the probability $P_{n+n'}$ that secondary electron emission can occur both in the photoionization process and in the subsequent Auger process by the approximation

$$P_{n+n'} \approx S_n \times A_{n'} \tag{11}$$

where $S_n$ is the calculated probability for shaking off $n$ electrons in the photoionization process and $A_{n'}$ is the observed probability for removing $n'$ secondary electrons due to the $KLL$ Auger process. (Note that the net effect of $P_{n+n'}$ on the loss of one secondary electron will be negative, since multiple events will deplete the number of single events.) In Table V are listed the various contributions to single-, double-, and triple-electron loss and their totals. Considering the approximations used, the agreement between calculation and experiment is very good. An accounting of the measured abundances of the more highly charged neon ions no longer presents a mystery.

## CONCLUSION

We have measured the relative abundances of ions resulting from the $K$ photoionization of Ne as a function of the photoelectron energy. From these measurements we have been able to examine various phenomena that can lead to self-ionization. One such phenomenon is electron shake-off that results from a sudden change in the effective charge as the photoelectron is ejected. Calculations have been made of the extent of this shake-off by use of the sudden approximation. When the velocity of the photoelectron is sufficiently high to ensure the validity of the sudden approximation, it has been possible, after subtracting the contribution of double-electron ejection in the $KLL$ Auger process, to successfully relate the measurements to these calculations. It has also been possible to qualitatively evaluate under what conditions the sudden approximation fails for electron shake-off. In contrast to electron shake-off, contributions to ionization arising from the phenomena of electron correlation and direct collision are not well understood. In this paper we have been able in some cases to set upper limits to these contributions, but more work both in theory and experiment are needed.

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