EXPERIMENTAL EVIDENCE FOR DOUBLE ELECTRON EMISSION IN AN AUGER PROCESS*

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(Received 13 January 1965)

An Auger process is generally described as a process in which a vacancy in an inner shell of an atom is filled by having one of the outer electrons drop into this hole, while a second outer electron goes into the continuum with the excess energy of the transition. Aside from the consequences of electron shake-off,[1,2] there has been neither theoretical discussion nor experimental evidence with regard to the ejection of more than one electron in an Auger process. In this paper, however, we shall give evidence for such an event following a *K* vacancy in neon.

In an earlier paper[3] we measured the relative abundances of ions produced by irradiation of neon at low pressures with 1.5-keV x rays. The results were interpreted in the following manner: (1) Singly charged neon represented ionization essentially in the *L* shell. (2) If a *K* vacancy occurred, an Auger process filled the hole in 99.3% of the cases and Ne^{2+} was formed. (3) Ions of higher charge gave evidence of secondary sources for electron emission. About 25% of the ions had charges greater than two.[4] Ionization as the result of a Coster-Kronig transition in the *L* shell of neon was ruled out because of energy considerations.[5] Calculations on electron shake-off following photoionization were, however, able to explain about two-thirds of the "excess" ionization, but there still remained an unaccountable source for secondary electron emission. To better understand the nature of this source, we have examined the charge spectrum of neon as a function of the energy of the incident x ray.[6] Of particular interest are the results from x rays of energies between 867 eV, the ionization energy for a 1*s* electron in neon, and about 913 eV, the energy required to remove a 2*p* as well as a 1*s* electron,[7,8] because, if x rays below about 913 eV cause photoelectron emission in the *K* shell of neon, any additional ionization that is observed must be attributed solely to the Auger process that fills the *K* vacancy.

The experimental results given in this paper are related to the charge spectrum of neon formed from ionization of x rays with energy between 867 and 913 eV. The general experimental procedure, which has been described elsewhere,[2] is to irradiate a rare gas with x rays in a specially designed mass spectrometer and to measure the relative abundances of the resulting ions. Gas pressures are sufficiently low that we can study the consequences of atoms undergoing photoionization in isolation without concerning ourselves with the additional complexities of ion-molecule reactions. The x rays used in the present experiment were the bremsstrahlung from a tungsten target. Data were taken as a function of the applied voltage on the x-ray tube from 1.60 to 0.85 keV. The uncertainty of the applied voltage was less than 0.5%. The x rays passed through a filter of 450 $\mu g/cm^2$ of Cu deposited on a film of 105 $\mu g/cm^2$ of polystyrene. This filter favors a high transmission just below 933 eV, so that most of the *K* vacancies were produced by x rays below this energy.

The relative abundance of neon ions resulting from x irradiation are shown in Table I, where E_{max} is the maximum energy of the bremsstrahlung. The errors quoted are from counting statistics. We note that the abundance of Ne^{3+} relative to Ne^{2+} is not strongly dependent on E_{max} because of the strong absorption of the Cu filter above 933 eV. The relative abundance of Ne^{1+} gives the relative amount of *L*/*K* photoionization, which is never overwhelming, even at 900 eV. The last experiment, where E_{max} is just below the *K* edge, illustrates the contribution of *L* photoionization alone. The data in Table I are corrected to obtain the final result we seek, viz., the abundance of Ne^{3+} relative to Ne^{2+} that has resulted from an initial *K* vacancy formed with x rays of energies below about 913 eV, for this will give us the relative amount of double electron emission accompanying the *KLL* Auger transition in neon. This final result is given for each experiment in the last column of Table II. In the first column of Table II we list the uncorrected abundances of Ne^{3+} relative to Ne^{2+}. The second column gives these data corrected for the contribution from photoionization in the *L* shell. The correction, which is quite

Table I. Relative abundances of neon ions formed as a function of x-ray energy spectra.[a]

Ion \ $E_{\max}$[b] (eV)	1600	1400	1200	1100	1000	930	900	850[c]
Ne^{1+}	39 ± 1	40 ± 3	45 ± 3	43 ± 3	53 ± 7	66 ± 8	110 ± 10	909 ± 91
Ne^{2+}	100 ± 1	100 ± 4	100 ± 4	100 ± 5	100 ± 7	100 ± 7	100 ± 6	100 ± 36
Ne^{3+}	10.2 ± 0.3	9.0 ± 1.1	8.8 ± 1.0	7.9 ± 1.5	11.7 ± 2.2	8.7 ± 1.2	8.3 ± 1.5	18 ± 18

[a] X rays are formed from a tungsten target and passed through a filter of 450-μg/cm^2 Cu on 105-μg/cm^2 polystyrene.

[b] Energy of electron striking tungsten target.

[c] Experiments with more transparent filters give the neon charge spectrum resulting for *L* ionization as $\mathrm{Ne}^{1+} = 725 \pm 4$; $\mathrm{Ne}^{2+} = 100 \pm 4$; $\mathrm{Ne}^{3+} = 5.4 \pm 0.7$.

small, is obtained by multiplying the abundance of Ne^{1+} by the charge spectrum for *L* photoelectron emission.[9] To obtain the final result, we made a correction for photoionization occuring with x rays of energies between $E_{\max}$ and 913 eV. This correction, which was also not large, since the Cu filter helped cut out contributions from the higher energy x rays, was estimated as follows:

$$\text{Correction} = \int_{913\ \text{eV}}^{E_{\max}} CI\mu T dE,$$

where C is the charge spectrum for neon,[10] I is the intensity of the x rays,[11] μ is the photoelectric cross section for neon, and T is the transmission of the filter; all the components of the equation are functions of the x-ray energy.

The weighted average for the values in the last column of Table II is 0.081 ± 0.008. The averaging process is artificial since the assignments of errors to the various corrections were somewhat arbitrary. However, the final results of the different experiments are internally consistent, and we give as the percent of double electron emission in the *KLL* Auger process of neon the value of $7.5 \pm 1.0\,\%$. This amount incidentally is consistent with the "missing" source of ionization mentioned earlier.[3]

Table II. Abundance of Ne^{3+} relative to Ne^{2+} as the result of *K* vacancies produced by x rays between the energies of 867 and 913 eV.

$E_{\max}$ (eV)	$\mathrm{Ne}^{3+}/\mathrm{Ne}^{2+}$ a	b	c
1600	0.102 ± 0.003	0.105 ± 0.003	0.071 ± 0.027
1400	0.090 ± 0.011	0.092 ± 0.011	0.066 ± 0.023
1200	0.088 ± 0.010	0.090 ± 0.010	0.075 ± 0.020
1100	0.079 ± 0.015	0.082 ± 0.015	0.068 ± 0.022
1000	0.117 ± 0.022	0.122 ± 0.023	0.123 ± 0.027
930	0.087 ± 0.012	0.082 ± 0.014	0.071 ± 0.015
900	0.083 ± 0.015	0.089 ± 0.016	0.089 ± 0.016
		Weighted average	0.081 ± 0.008

[a] Uncorrected data from Table I.

[b] Data corrected for *L* photoelectron emission.

[c] Data fully corrected for *L* photoelectron emission and for contribution from x rays of energies above 913 eV.

In seeking the reason for double ionization in the Auger process, we have examined the possibility of electron shake-off due to changes in the effective charge as the result of atomic readjustment. This contribution can be calculated from the sudden approximation by use of the equation

$$P = 1 - \left| \int \psi_f^* \psi_i d\tau \right|^2,$$

where P is the probability for an electron to vacate its shell and ψ_i and ψ_f are the initial and final states of the Auger process.[12] The results of such a calculation gave 0.5 % as an upper limit to the amount of electron shake-off, which is small compared to the 7.5 % observed for double ionization.

The cause for the bulk of the double electron emission probably resides in the phenomena of electron correlation.[13] Extra ionization in addition to the primary process has also been observed with photoelectron emission.[14-16] Note, for example,[9] that multiple ionization has occurred in the photoelectron emission of the *L* shell, since one expects only charge-one neon. The measured abundances for Ne^{2+} and Ne^{3+} give evidence for single and double secondary-electron emission, and again calculations based on electron shake-off account for only a portion of the observed extra ionization.[16] Furthermore, if we compare Ne^{2+} from

L photoionization with Ne^{3+} from a K vacancy followed by a KLL Auger process, we note that the probability for losing one "extra" electron is about the same. Likewise, if we compare Ne^{3+} from L photoionization with Ne^{4+} from the KLL Auger process,[17] we see that the probability for losing two extra electrons is also about the same. These observations might be understood if we consider that in both the case of L photoionization and that of the KLL Auger process we are dealing with electron correlation between the ejected electron (in both events it is ejected from the L shell) and other electrons of the L shell of neon. In future publications we hope to examine for both phenomena the relationship between multiple ionization and electron correlation.

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

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

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

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

[4] This result, which is about 5 % lower than our reported value, was taken with our present spectrometer and is more accurate.

[5] The transition following a $2s$ hole as the result of a KLL Auger process is endothermic by about 40 eV (cf. reference 3, p. A389).

[6] T. A. Carlson and M. O. Krause: The complete results of this study will be published later.

[7] The ionization potential for Ne^{1+} with a $1s$ hole has been obtained (1) from a Hartree-Fock solution for Ne^{1+} with the proper configuration (49 eV), and (2) by interpolating between the ionization potential for Na II and Ne I with the help of Slater's rules for screening constants (43 eV). We take 46 eV as our best estimate.

[8] One might conceive that it would be energetically possible to put a $2p$ electron into an excited state in conjunction with photoelectron emission so long as the x-ray energies were above about 900 eV. Then, if a $2s$ vacancy were later found in the KLL Auger process, a Coster-Kronig transition including the excited electron might be possible. The probability for the overall process should be small, and in any case would be eliminated in our measurement at 900 eV.

[9] $Ne^{1+} = 100$; $Ne^{2+} = 13.8$; $Ne^{3+} = 0.74$ (T. A. Carlson, unpublished data). Incidentally, one might note that multiple ionization is also present in the L photoelectron emission, since only the singly-charged ion is expected. Ne^{2+} and Ne^{3+} are evidence for the emission of one or two "extra" electrons. (In the case of a K vacancy followed by a KLL Auger process, the emission of one or two "extra" electrons gives Ne^{3+} or Ne^{4+}, respectively.) For a comparison of multiple ionization from photoionization in the L shell with that from the KLL Auger process, see the last paragraph of this paper.

[10] This charge spectrum has been measured using characteristic x rays with energies from 17.5 to 0.932 keV. See reference 6. For x rays between the energies of 913 and 932 eV we used the data taken with the Cu $L\alpha$ line (932 eV).

[11] H. Neff, Z. Physik 131, 1 (1951).

[12] The Hartree-Fock solutions to the wave functions have been computed for $Ne^{1+}(1s, 2s^2, 2p^6)$ and $Ne^{2+}(1s^2, 2s^2, 2p^4)$ from a code by Charlotte Froese. For discussion of calculation of electron shake-off following an Auger process, see references 1 and 2.

[13] 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.

[14] H. W. Schnopper, Phys. Rev. 131, 1558 (1963).

[15] C. Bonnelle and F. Wuilleumier, Compt. Rend. Acad. Sci. (France) 256, 5106 (1963).

[16] T. A. Carlson, to be published.

[17] In addition to the results on Ne^{3+}, we have obtained data on Ne^{4+}. After correcting the data, we find Ne^{4+}/Ne^{2+} to be about 0.004 under conditions where the excess ionization is solely due to the energy available from the Auger process.