Charge Distributions of Krypton Ions Following Photo-Ionization in the *M* Shell*

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Charge distributions of krypton ions that result from ionization in the *M* shell by x rays have been measured with a magnetic mass spectrometer. X-ray energies ranged from 100 to 1400 eV. The following results are derived from the charge spectra: (a) In filling a hole in the *3d* shell, an Auger process which generates two continuum electrons competes strongly with the common Auger process which generates one continuum electron. This so-called double Auger process occurs in $(31\pm4)\%$ of the events. (b) The Coster-Kronig transitions *3p–3dN* and *3p–3d3d* have nearly equal intensities. (c) Partial photoabsorption coefficients for *M* electrons are poorly predicted by the Stobbe-Hall formula even for energies above 1 keV. Calculated shake-off probabilities of *M* and *N* electrons are given for the sudden removal of a *3s*, *3p*, or *3d* electron.

INTRODUCTION

As has been shown earlier,[1–4] the reorganization of an atom ionized in an inner shell can be described in terms of radiative, radiationless, and electron shake-off processes. To recapitulate, a hole is filled either in a radiative transition with the emission of a quantum or in an Auger transition with the emission of an electron. In addition, electrons are released in the shake-off process which can occur when the atomic Coulomb field changes abruptly; this means electron shake-off may accompany both photoelectron emission and Auger events. A multiply charged ion arises because, as a rule, radiationless processes play a predominant part in the deexcitation of the atom, and because Auger transitions often occur in succession generating a vacancy cascade.[2] According to the probabilities of the routes by which the atom reorganizes, a charge distribution is produced for a given initial vacancy or vacancy distribution.

These charge distributions are of interest in various fields such as gaseous electronics, atomic collisions, radiation damage, and x-ray satellites. They also offer a useful probe for processes active in the reorganization and for the initial ionization event itself. Consider, for example, the following cases that are presented in this study: (a) double electron emission in an Auger process filling a *3d* hole in krypton, (b) relative intensities of two competing Coster-Kronig transitions to the *3p* level, and (c) evaluation of relative partial photoabsorption cross sections of *M* electrons.

Auger transitions to the *3d* level can be investigated easily by observing the charge states of the readjusted atom since radiative transitions are negligible. Charge two arises from the ordinary or single Auger process[5] *3d-NN*, and charge three from the double Auger process *3d-NNN*. The latter process, in which two electrons are ejected, has been observed previously for the analogous transitions *K-LLL* in neon[6] and *2p-MMM* in argon,[7] and it is the primary aim of this work to demonstrate the presence of this process in krypton and to measure its intensity relative to the single Auger process.

The transitions *3p-3dN* and *3p-3d3d*, both of the Coster-Kronig type, compete in filling a *3p* vacancy and lead with subsequent *3d-NN* to triply and quadruply charged ions. The abundances of Kr^{3+} and Kr^{4+} are, therefore, a measure of their relative intensities. The transition *3p-3d3d* has previously[8] escaped detection in electron-energy analysis because of the small energy of the *3p-3d3d* Auger electron. Charge spectrometry should, however, render an approximate value for its relative intensity despite some inherent complications.

The dependence of charge spectra on the initial vacancy distribution allows, in the case of excitation by x rays, evaluation of relative partial photoabsorption cross sections. For photon energies from 220 to 1100 eV, values of the ratio $\sigma_{3p}:\sigma_{3d}$ can be derived and compared with recent calculations[9]; and for energies of 850 and 1150 eV, values of $\sigma_{3s}:\sigma_M$, which have not been calculated, can be estimated with a fair degree of reliability.

EXPERIMENTAL

Apparatus and method have previously been described in detail.[4] Briefly, krypton was irradiated at

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

[1] R. H. Rubenstein, thesis, University of Illinois, 1955 (unpublished).

[2] A. H. Snell and F. Pleasonton, J. Phys. Chem. **62**, 1377 (1958).

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

[4] T. A. Carlson and M. O. Krause, Phys. Rev. **137**, A1655 (1965); **140**, A1057 (1965).

[5] The left term of a transition, i.e., *K-LL* or *K-LLL*, designates the initial vacancy or vacancies, the right term designates final vacancies. For the shortest presentation, we sacrifice uniformity of symbols and denote atomic states by those symbols that are sufficient for a particular case.

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

[7] T. A. Carlson and M. O. Krause, Bull. Am. Phys. Soc. **10**, 455 (1965).

[8] W. Mehlhorn, Z. Physik **178**, 21 (1965).

[9] J. W. Cooper (private communication). We thank Dr. J. Cooper for permitting us to use his calculations prior to publication.

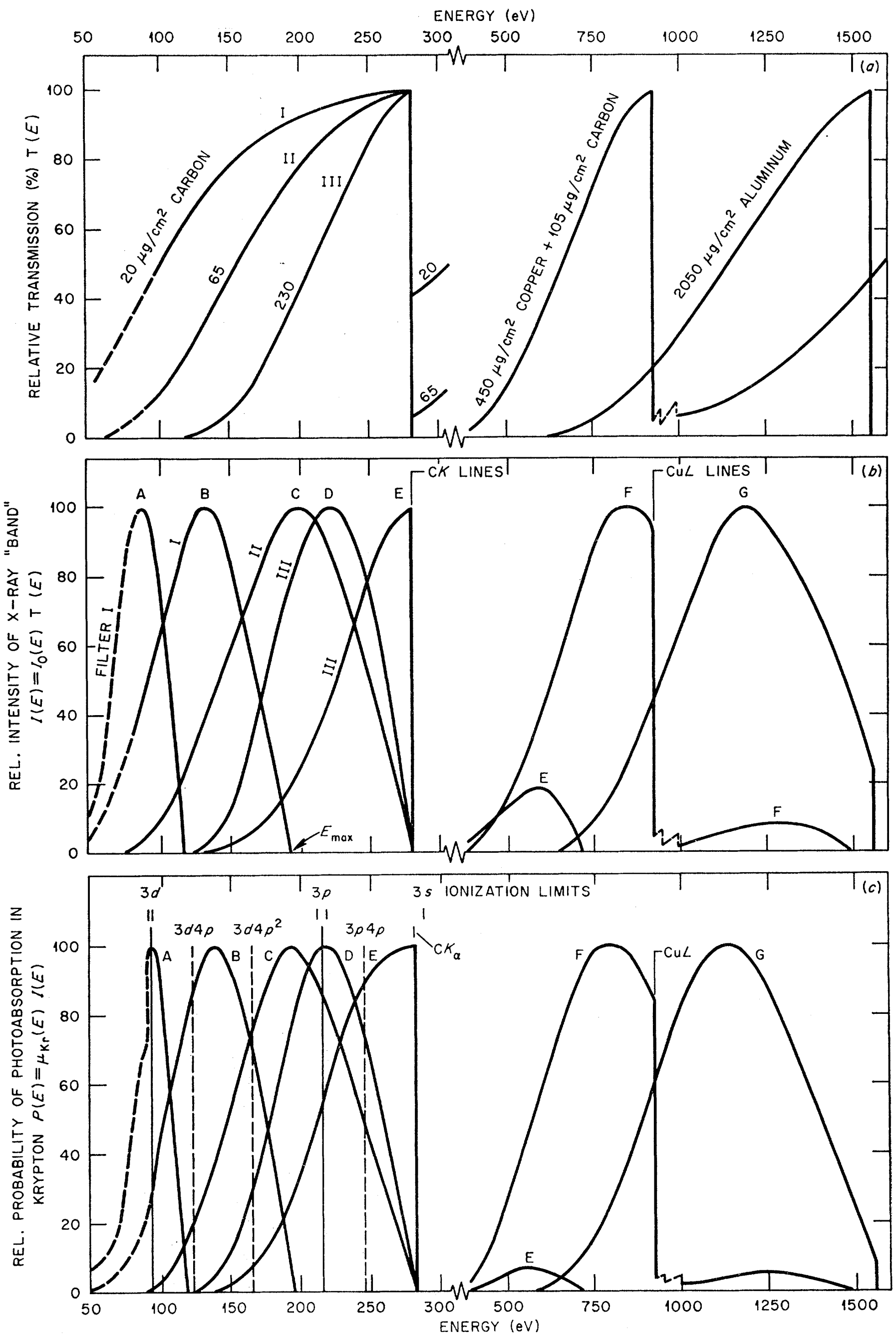

FIG. 1. (a) Relative transmission curves for various filters. Thicknesses of filters are known within ±5%, except for filters I (±20%) and II (±10%). Filters I to III are polystyrene filters: μ(polystyrene) $\approx\mu$(carbon). (b) X-ray distributions $I(E)$ transmitted through filters. Curves normalized at peak values of bremsstrahlung. (c) Effective x-ray distributions, showing the relative number of vacancies formed in krypton by x rays of $I(E)$ as a function of energy.

low pressures by x rays from various targets. Ions formed in the source volume of the spectrometer were extracted by a small electric field, accelerated toward a magnetic analyzer, and detected by a dynode structure.

Bremsstrahlung from a tungsten anode was used for most experiments. The energy range of x rays was controlled by the operating (dc) voltage of the x-ray tube and absorption characteristics of different filters which separated the x-ray tube from the gas chamber.

Figure 1(a) shows calculated x-ray transmission curves $T(E)$ for polystyrene filters of various thicknesses, Fig. 1(b) shows energy spectra $I(E)$ of transmitted x rays as used in the experiment, and Fig. 1(c) shows the relative number $P(E)$ of vacancies produced by x rays of energy E of the given energy distributions $I(E)$. With the exception of curve G in Fig. 1 these curves should be understood as idealized representations, since experimental values are not available in literature

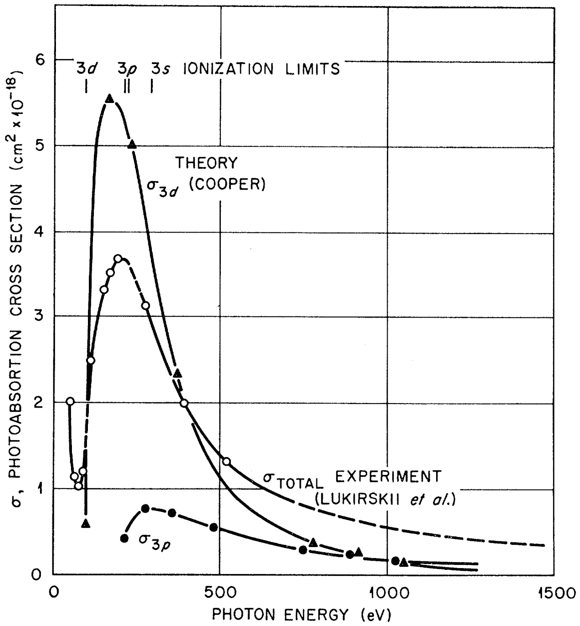

FIG. 2. Total absorption cross section of krypton according to Lukirskii *et al.* (Ref. 15) and partial photoabsorption cross sections according to Cooper (Refs. 9 and 16).

for the mass absorption coefficients of carbon below the K edge and copper below the L edge, and for bremsstrahlung spectra produced by electrons of less than 900-eV energy. Instead of obtaining the desired mass absorption coefficients from universal absorption functions by introducing reasonable values for absorption jumps (Jönsson's method[10]) or for "critical" wavelengths (method of Henke *et al.*[11]) at the respective edges, we preferred to use measured coefficients of neon[11,12] as the basis for estimating μ of carbon and copper. We regarded the ratios $\mu_{\text{carbon}}/\mu_{\text{neon}}$ and $\mu_{\text{copper}}/\mu_{\text{neon}}$ as being constant over the range from about 100 to 900 eV, except for the intervals between the K edges of neon and carbon, and the K edge of neon and L edges of copper. Values thus found should be rather good,[13] perhaps within $\pm 15\%$, even for energies as low as 100 eV. To obtain bremsstrahlung spectra for incident electrons of less than 900-eV energy we drew curves similar to those measured by Neff[14] for energies greater than 900 eV, that is, we surmised that the relation $I_\nu = \text{const}(\nu_0 - \nu)$ holds also in this region of small energies.[14a] A possible deviation from this linear relationship below about $0.6\nu_0$ of the high-frequency cutoff ν_0, as indicated in Neff's curves, would not introduce a serious error in calculating the transmitted x-ray spectrum $I(E)T(E)$, since the absorption $[1-T(E)]$ of the chosen filters becomes determining toward the lower energies. The family of curves $P(E)$ of Fig. 1(c) was obtained by multiplying $I(E)T(E)$ with the atomic absorption coefficient of krypton as reported by Lukirskii *et al.*[15] In Fig. 1(c) positions of the ionization limits of $3s$, $3p$, and $3d$ electrons are marked as well as those corresponding to the additional ionization of one or two $4p$ electrons. Thus Fig. 1 shows which initial ionization processes are energetically possible for a given distribution $P(E)$. Relative probabilities of these processes will be discussed in the next sections. The absorption curve of Lukirskii *et al.* is plotted in Fig. 2, together with Cooper's[9,16] recently calculated partial absorption cross sections of $3p$ and $3d$ electrons.

With the exception of one experiment, run D, the x-ray flux through the gas chamber was so small that the pressure in the source volume had to be raised to about 4×10^{-5} Torr to assure satisfactory counting rates of more than 5 counts/min. Although the pressure in the analyzer was lower by a factor of about 5, charge-exchange processes in collisions could not be neglected and the data needed to be corrected. Correction factors were determined experimentally by measuring relative abundances of the ions as a function of pressure. With charge 2 as reference, these factors were for $p=4\times10^{-5}$ Torr as follows: Kr^{1+}, 0.86; Kr^{3+}, 1.05; Kr^{4+}, 1.10; Kr^{5+}, 1.15; Kr^{6+}, 1.21.

Since N_2^+ and N^+ coincide with Kr^{3+} and Kr^{6+} on the m/e scale, contamination by nitrogen ions needed to be determined by bombarding the residual gas with x rays of the same energy as in the experiment. Contributions of these ions were found insignificant for all runs, except runs A and B with less than 5% of the abundance of $m/e=28$ being due to N_2^+. Nitrogen contamination of the krypton sample was negligibly small.

Data in the following sections represent averages from at least 3 runs each, and have been corrected for pressure effects, and contributions of ions from the residual gas. Errors quoted account for statistical errors and uncertainties in the corrections. Variation of the detector response with charge, and ionization by spurious electrons were negligibly small for all charges but charge one. These corrections for Kr^{1+}, estimated to be less than 20% of the measured intensity, were omitted.

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[10] See A. H. Compton and S. K. Allison, *X-rays in Theory and Experiment* (D. Van Nostrand Inc., New York, 1935), p. 537.

[11] B. L. Henke, R. White, and B. Lundberg, J. Appl. Phys. **28**, 98 (1957).

[12] D. L. Ederer and D. M. Tomboulian, Phys. Rev. **133**, A1528 (1964).

[13] Values of μ for nitrogen and oxygen at 44.5 Å and 68 Å offer additional test points (see Ref. 11).

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

[14a] *Note added in proof.* Although measurements of F. J. Peterson, Jr., and D. H. Tomboulian, Phys. Rev. **125**, 235 (1962) and calculations of P. Kirkpatrick and L. Wiedmann, *ibid.* **67**, 321 (1945) show that this assumption is not quite correct, the x-ray spectra of Fig. 1 are only very slightly affected.

[15] A. P. Lukirskii, I. A. Brytov, and T. M. Zimkina, Opt. i Spektroskopiya **17**, 438 (1964) [English transl.: Opt. Spectry. (USSR) **17**, 234 (1964)].

[16] These curves were calculated without considering exchange effects, which, according to Cooper (private communication), would somewhat smear out the curves.

TABLE I. Charge distributions of ions resulting from photoabsorption primarily in the $3d$ shell of krypton.[a]

	Run A	Run B
Target	W	W
E_{max} (eV)	120±2	195±10
Kr^{1+}	18±6	5.5±2.6
Kr^{2+}	69±5	65.1±3.2
Kr^{3+}	31±3	35.0±2.2

[a] Relative abundance I_n of charge n is given in this and the following tables to make $\sum_{n=2}^{m} I_n = 100$ and $I_1 = I_1^*/\sum_{n=1}^{m} I_n^*$, where $\sum_{n=1}^{m} I_n^* = 100$.

RESULTS AND DISCUSSION

A. Double Electron Emission in an Auger Process Filling a 3d Vacancy

Charge spectra listed in Table I were produced by x rays of distributions A and B of Fig. 1. They arise largely from readjustment to a $3d$ vacancy, and we correlate doubly and triply charged ions with the single Auger process $3d$-NN and the double Auger process $3d$-NNN. Before assigning the abundances of Kr^{2+} and Kr^{3+} entirely to these Auger events, let us consider other ionization processes which may lead to the same charge states: (a) transitions $3d$-$4s4p$ and $3d$-$4s4s$ with subsequent $4s$-$4p4p$; (b) Auger transition $3d$-$4s4s$ with subsequent configuration interaction[17] $4s^04p^6 \rightarrow 4s^24p^3$; (c) photoejection of a $3d$ electron and shake-off of an N electron with subsequent Auger transitions; (d) direct multiple photo-ionization in the N shell.

The Coster-Kronig transition $4s$-$4p4p$ is endothermic by about 26 eV when an additional hole in the $4s$ or $4p$ level is present. The energy difference of the configurations $4s^04p^6$ and $4s^24p^3$ is negative by about 3 eV according to one Hartree-Fock calculation[18] and positive by about 3 eV according to another[17]; it is, however, negative by 13 eV according to $E(4s^24p^3)=75.5$ eV from Moore's tables[19] and $E(4s^04p^6)=62.8$ eV from Mehlhorn's measurements.[8] Therefore, processes (a) and (b) can be ruled out unless one of the N electrons has been excited into a bound state close to the continuum in the preceding transition $3d$-$4s4s$ or $3d$-$4s4p$. Such a process, $3d^94s^24p^6 \rightarrow 3d^{10}4s4p^4np$, can be considered a special case of the double Auger process $3d^94s^24p^6 \rightarrow 3d^{10}4s4p^4$, and by observing only the charge states of the atom, we cannot distinguish between ejection of a second electron and excitation to an auto-ionization level. We include the possibility of excitation in the double Auger process, in which *two* electrons share the energy of the transition. Process (c) does not apply to run A since none of the photons had sufficient energy to ionize both a $3d$ and an N electron. For run B we estimate[4] this process to occur in about 3% of the cases, and this figure corresponds roughly to the slight shift in the relative intensities of charge two and three from run A to run B. With this shift accounted for, and noting the large difference of the abundances of Kr^{1+} between spectra A and B, it seems that multiple photo-ionization in the N shell contributes little to charge states two and three.

Since no other ionization processes are indicated in filling a $3d$ hole but Auger events we derive from the charge spectrum of run A a relative probability of 0.31 ± 0.04 for the double Auger process. This value is much larger than the values of 0.08 and 0.10 for the K-LLL transition in neon[5] and the $2p$-MMM transition in argon.[7] Although we cannot clarify the nature of the double Auger process by the present experiment we can now recognize the following trend: Comparing the data of neon, argon, and krypton, we see that deexcitation of the atom by a double Auger process becomes more frequent with decreasing energy of the outgoing Auger electrons. This observation can be related with some reservation to a calculation by Callan *et al.*[20] which indicates a rapid increase of the values $|R|$ of the radial electrostatic overlap integrals with decreasing energy of the free electrons for K-LL and $2s$-$2p3d$ transitions. If we surmise a similar behavior for other transitions and ignore differences in the wave functions between a doubly and a triply ionized atom we can conceive that the combined probability of ejecting two slow electrons, perhaps of 5- and 10-eV energy as for krypton, may become quite large compared with the probability of removing one single faster electron.

B. Relative Intensities of the Coster-Kronig Transitions 3p-3d3d and 3p-3dN

Table II lists experimental charge spectra produced by x rays of distributions C, D, and E, together with calculated spectra. To determine the intensity ratio of the two competing Coster-Kronig transitions $3p$-$3d3d$ and $3p$-$3dN$, we need to consider Kr^{2+}, Kr^{3+}, and Kr^{4+}. Kr^{2+} comes from Auger transitions $3d$-NN and $3p$-NN; Kr^{3+} from $3p$-$3dN$, $3d$-NNN and possibly $3p$-NNN; Kr^{4+} from $3p$-$3d3d$ and perhaps $3p$-$3dNN$. Furthermore, when photoelectron emission is accompanied by shake-off of one or more electrons, a multiply ionized atom is formed, for example $3dN$, and subsequent Auger transitions $3dN$-NNN and $3pN$-NNN lead also to Kr^{3+}, and $3pN$-$3dNN$ and $3dNN$-$(N)^4$ lead to Kr^{4+}.

We used for relative rates of the transition $3d$-NN and $3d$-NNN values from the preceding section, for

[17] This mechanism was suggested by J. W. Cooper (private communication). We believe, however, that dipole transitions $4p \rightarrow 4s$ would be more probable than this second-order process, even if it were energetically allowed.

[18] Obtained with a code written by Charlotte Froese, Can. J. Phys. 41, 1895 (1963).

[19] *Atomic Energy Levels*, edited by C. F. Moore, Natl. Bur. Std. (U. S.) Circ. No. 467 (U. S. Government Publishing and Printing Office, Washington D. C., 1952), Vol. 2.

[20] E. J. Callan, P. Nikolas, and W. L. McDavid, *Proceedings of the Third International Conference on Physics of Electronic and Atomic Collisions, London, 1963* (North-Holland Publishing Company, Amsterdam, 1964), p. 348.

TABLE II. Charge distribution of ions resulting from photoabsorption in the $3p$ and $3d$ shells of krypton.[a] Comparison of experimental data with calculated charge spectra: I, from Auger processes with[b] $I_{1,2}=0$ and electron shakeoff; II, from Auger processes alone with $I_{1,2}=1$; III, from Auger processes with $I_{1,2}=1$ and electron shakeoff. Initial vacancy distributions[c]: Run C: $3p$ shell 5%; $3d$ shell 95%. Run D: $3p$ shell 8%; $3d$ shell 92%. Run E: $3p$ shell 16%; $3d$ shell 83% ($3s$ shell ≈ 1%)[d].

Charge of ion	Run C, W target $E_{max}=285\pm10$ eV, P_{max} at 195 eV Expt	Calculated I	II	III	Run D, W target $E_{max}=285\pm10$ eV, P_{max} at 220 eV Expt	Calculated I	II	III	Run E, C target $E_{max}=720\pm20$ eV, P_{max} at 290 eV Expt	Calculated I	II	III
1	6.5±0.7	···	···	···	2.5±1.6	···	···	···	2.5±0.6	···	···	···
2	57.1±2	61.5	66.6	61.5	56.6±2.3	59.0	64.3	59.0	51.9±0.5	53.4	59.0	53.4
3	40.2±2.1	38.4	31.8	36.2	39 ±1.2	40.8	32.1	37.2	39.8±0.6	45.9	33.4	38.7
4	2.9±0.7	0.1	2.2	2.3	4.5±0.5	0.2	3.6	3.8	7.5±0.3	0.6	7.5	7.7
5	···	···	···	···	···	···	···	···	0.7±0.2	<0.1	0.1	0.2

[a] See note (a) of Table I.
[b] $I_{1,2}$ denotes the intensity ratio of $3p$-$3d3d$/$3p$-$3dN$.
[c] Absorption in the N shell excluded.
[d] Charge distribution of Table IV column 8 used for $3s$ vacancy.

$3p$-NN a probability[1,8] of 10% of all transitions originating in the $3p$ level, and we neglected the potential double Auger processes[21] $3p$-NNN and $3p$-$3dNN$. We determined the distribution of initial $3p$ and $3d$ vacancies from the curves of Fig. 1(c) and Fig. 2 by using the cross section ratio $\sigma_{3p}:\sigma_{3d}=15:85$ as an average value. To find the relative number of initial double vacancies we relied on the calculated shakeoff probabilities of Table V, adjusted for the fraction of photons above the corresponding thresholds and for the velocities of the outgoing photoelectrons.[4] This adjustment gave the following values in percent of the corresponding single vacancy for runs C, D, and E: $3dN$ holes: 6.5, 8, and 9; $3dNN$ holes: 0.1, 0.2, and 0.3; $3pN$ holes: 0.1, 0.1, and 0.6.

Instead of calculating the intensity ratio of $3p$-$3d3d$/$3p$-$3dN$ for each run from a set of equations, we calculated charge spectra for three different cases to show how extreme values of this ratio and inclusion or exclusion of electron shakeoff affect the charge distributions. The resulting spectra are summarized in Table II. While agreement with experiment is poor for spectra I and II, it is quite satisfactory for all runs and all charge states for spectra III. The comparison indicates that transition rates of the two Coster-Kronig transitions are equal within an estimated error[21] of ±25%. It also shows that the value of the ratio $\sigma_{3p}:\sigma_{3d}$, a variable in the calculation of the charge spectra, is approximately 15:85 as given by Cooper's calculation. The data did not allow improving this value in view of the uncertainties in x-ray distributions, shakeoff probabilities, and Auger transition rates.

TABLE III. Charge distribution of ions resulting from absorption of 850 and 1150-eV photons in the M shell of krypton.[a] Comparison of experimental and calculated charge spectra. Initial vacancy distributions[b]: Run F: $3d$ shell 54%; $3p$ shell 34%; $3s$ shell 12%. Run G: $3d$ shell 34%; $3p$ shell 47%; $3s$ shell 19%.

Charge of ion	Run F, Cu target P_{max} at about 850 eV Expt	Calculated[d]	Run G, W target[c] P_{max} at about 1150 eV Expt	Calculated[d]
1	5±1.5	···	3 ±0.5	···
2	37.7±1.6	37.4	27.5±1.6	27.3
3	39.1±1.3	39.6	40.8±1.5	40.0
4	17.6±1.0	19.3	22.9±0.9	26.7
5	4.3±0.4	3.4	7.2±0.5	5.4
6	1.2±0.5	0.4	1.3±0.5	0.6

[a] See note (a) of Table I.
[b] Absorption in the N shell excluded. According to a modified Stobbe-Hall formula (Ref. 22) one would obtain the following vacancy distributions for run F: 9%, 85%, 6%, and for run G: 7%, 86%, 7%.
[c] X rays from an Al target produce essentially the same charge distribution.
[d] Including electron shakeoff from $3d$, $4s$, and $4p$ shells.

C. Charge Spectra Resulting from Ionization in the M Shell by X Rays of Energies from 600 to 1400 eV

X rays of energy distributions F and G were used to produce vacancies not only in the $3d$ and $3p$ shells but also in the $3s$ shell. Experimental results are summarized in Table III together with calculated charge spectra. The relative abundance of Kr^{2+} is still quite large, even under these conditions, indicating that at least 30% of the x rays are absorbed by $3d$ electrons. This reflects the unusual photoabsorption characteristics in the M shell of krypton, which have been described earlier by Lukirskii *et al.*[15] and Cooper.[9] It is inconsistent with the small photoabsorption cross section σ_{3d} of about 8% of total M shell absorption which is predicted by the modified Stobbe-Hall formula.[22] Obviously, screened hydrogenic wave functions are inadequate to compute absorption cross sections satisfactorily in this region of soft x rays.

To check whether values of the ratio σ_{3p}/σ_{3d} taken from Fig. 2 are compatible with charge spectra F and G, and to evaluate σ_{3s}/σ_M, we calculated charge spectra

[21] Even if the transition $3p$-NNN would have half the intensity of the "parent" transition $3p$-NN it would have little bearing on the charge distributions. The intensity ratio $3p$-$3dNN$/$3p$-$3dN$ presumably is smaller than 0.15; this value has been considered in estimating the error of the relative intensities of the Coster-Kronig transitions.

[22] H. Hall, Rev. Mod. Phys. 8, 358 (1936). Alan J. Bearden, University of California, San Diego, report, 1965 (unpublished).

TABLE IV. Relative number of electrons lost (in %) as the result of an initial single vacancy in the M shell or multiple vacancies in the M and N shells of krypton.

Initial vacancies / Number[a] of electrons lost	$3d$	$3dN$	$3dNN$ or $3d3d$	$3p$	$3pN$	$3pNN$ or $3p3d$	$3s$	$3sN$	$3sNN$	$3s3d$	$3s3p$
2	69	...	...	10	...	...	15.2	...	...	...	...
3	31	100	...	45	10	...	46.5	14.6	...	...	...
4	...	...	100	45	45	10	27.3	45.9	14.4	15.2	1.6
5	...	...	...	...	45	90[b]	11.0	27.7	45.2	46.5	19.1
6	...	...	...	...	...	...	...	11.8	41.3[b]	38.3[b]	47.8
7	...	...	...	...	...	...	...	...	...	...	31.5
Source	This paper Sec. A; Table I			This paper Sec. B, Table II See also Refs. 1,8			Rubenstein (Ref. 1) and results of Secs. A and B				

[a] Photoelectron included.
[b] Assuming that $3p$-$3d3d$ becomes energetically forbidden.

by referring to the experimental abundance of Kr^{2+}. We obtained the initial vacancy distribution, representative of the partial absorption coefficients, as follows: In accordance with the spectra of Table IV and shake-off probabilities of Table V we varied the relative number of $3d$ vacancies to fit the observed abundance of Kr^{2+}. The percentage of $3p$ vacancies was then obtained from the curves σ_{3p} and σ_{3d} of Fig. 2, and the percentage of $3s$ vacancies was given as the remainder. With the resulting vacancy distributions, listed in Table III, satisfactory agreement could be achieved between calculated and observed charge spectra for both runs. This supports theoretical values of σ_{3p}/σ_{3d} and it indicates that about 12% of 850-eV photons and about 19% of 1150-eV photons are absorbed by $3s$ electrons.

D. Electron Losses in the Reorganization of the Krypton Atom

In Table IV, electron-loss distributions or charge spectra are given for initial vacancies in the $3d$, $3p$, or $3s$ shell of krypton. Also listed are charge distributions for initial multiple vacancies, designated as $3dN$, $3dNN$, etc. Thus, for any given distribution of initial vacancies, charge spectra can readily be calculated by superimposing these individual spectra.

Entries in Table IV were obtained from the data of Secs. A and B, and, in the case of $3s$ vacancies, from Rubenstein's $3s$-XY rates.[1,8] In calculating the distributions we assumed an orderly stepwise propagation of holes, produced by Auger processes, toward the outer shell. We also assumed that transition rates per electron available remained constant. There are two exceptions, however. The double Auger process $3d$-NNN becomes energetically forbidden in an atom already ionized in the N shell and the transition $3p$-$3d3d$ is probably suppressed when more than two N electrons have previously been removed, causing a slightly stronger binding of $3d$ electrons.

TABLE. V. Probabilities of removing an electron from the M and N shell as a consequence of the sudden creation of a $3s$, $3p$, or $3d$ hole.

Initial hole / State vacated	Probabilities in % $3s$	$3p$	$3d$
$4p$	10.7	10.6	10.3
$4s$	1.4	1.6	1.6
$3d$	0.8	0.9	0.7
$3p$	0.1	0.1	0.1
$3s$	0.01	0.01	0.02
Total	13.0	13.2	12.7

E. Electron Shake-off

Electron shake-off[23] occurs when the Coulombic field of the atom is changed abruptly. Photoelectric ejection of an electron, for example, can cause such a sudden change. Then the probability of removing another orbital electron in the state n, l is given according to the sudden perturbation theory by

$$P_{n,l}=1-\left|\int \psi_f^*(Z_{\text{eff}}+\Delta Z_{\text{eff}})\psi_i(Z_{\text{eff}})d\tau\right|^2,$$

where $\psi_i(Z_{\text{eff}})$ and $\psi_f(Z_{\text{eff}}+\Delta Z_{\text{eff}})$ represent the initial and final states of the n, l electron and ΔZ_{eff} is the change in effective charge caused by the removal of an inner electron. We used Hartree-Fock wave functions[18] to calculate shake-off probabilities pertinent to this study. Results are summarized in Table V and quoted numbers consider all electrons present in states n, l. Usually only few electrons are excited into bound states so that the given values very nearly represent ionization probabilities.

We used the shake-off probabilities listed in Table V without corrections for runs F and G, since in these cases photoelectrons leave the atom fast enough to justify the application of the above expression. For runs C to E, however, the condition of suddenness is not

[23] E. L. Feinberg, J. Phys. (USSR) 4, 423 (1941); see also Ref. 4 for further citations.

fulfilled, and we reduced the probabilities by empirical factors gained from measurements of neon.[4]

CONCLUSIONS

By measuring relative abundances of multiply charged ions of krypton, produced by x-ray bombardment, we were able to demonstrate the existence of the double Auger process *3d-NNN* in which two electrons are ejected. Such a process has previously been observed in neon and argon for transitions to the outermost shells, but in the case of krypton an unusually large intensity of 0.3 relative to the single Auger process was obtained. It seems that the double Auger process competes strongly with the single Auger process when the outgoing electrons have small energies and originate from the outer atomic shell. We also could deduce from our data that the two Coster-Kronig transitions *3p-3d3d* and *3p-3dN* occur with about equal frequency. We showed further that the Stobbe-Hall theory poorly predicts partial absorption cross sections for M electrons in krypton even for photon energies as high as 1100 eV.

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Low-Energy e^--Ar Total Scattering Cross Sections: The Ramsauer-Townsend Effect*

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The Ramsauer technique has been used to measure absolute total e^--Ar scattering cross sections from 0.1 to 21.6 eV with an estimated probable error of $\pm 3\%$. A phase-shift analysis of the data (for the $l=0,1,2$ partial waves) has been made using "modified effective range" theory which yields a scattering length of $-1.65\ a_0$ and a minimum total cross section of 0.125 Å^2 at 0.285 eV.

INTRODUCTION

The transparency of the heavy rare gases to low-energy electrons was discovered independently by Ramsauer[1] and Townsend and Bailey,[2] and is usually referred to as the Ramsauer-Townsend effect.[3] Holtsmark[4] was able to qualitatively explain the effect by empirically introducing an attractive long-range polarization potential with a variable small-distance cutoff parameter in connection with a Hartree field representation of the Ar atom. Thus the Ramsauer-Townsend effect can be explained (at least qualitatively) in terms of potential scattering. Alternatively this effect may be thought of as being a diffraction effect with the "size" of the target atom being determined by the polarizability of the system of the incoming electron plus the target atom.

O'Malley[5] has recently applied effective-range theory[6] to approximate determinations of electron–rare-gas scattering lengths from the data of Ramsauer and Kollath.[7] However, in the case of Ar, the cross section does not vary sufficiently[7] over the measured range of electron energies[5] to give a very sensitive determination of either the scattering length or the effective range of the polarization potential. The latter quantity would be of much value in the prediction of electron-atom scattering cross sections. Furthermore, the previous direct measurements in Ar which show a Ramsauer-Townsend minimum, of Ramsauer and Kollath,[7] Rusch,[8] and Normand,[9] disagree with each other by as much as a factor of 2.8 as to the cross section at the minimum and a factor of 2 as to the energy at the minimum.[10]

Therefore, it was decided to make precise direct measurements of the total electron–argon-atom scattering cross section to lower values of incident electron energy than were previously possible.

APPARATUS AND PROCEDURE

The apparatus and procedure are the same as those described previously for Ramsauer-type measurements

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