Vacancy Cascade in the Reorganization of Krypton Ionized in an Inner Shell*

MANFRED O. KRAUSE AND THOMAS A. CARLSON
Oak Ridge National Laboratory, Oak Ridge, Tennessee
(Received 10 November 1966)

Charge distributions of krypton ions following ionization in the $1s$, $2s$, or $2p$ shell are calculated under the assumption that reorganization occurs by successive steps in a vacancy cascade in which Auger and radiative transitions partake. These distributions compare favorably with experimental charge spectra arising from photo-ionization in the K or L shell (this paper), from electron capture in ^{79}Kr, and from β decay in ^{85}Kr (Snell and Pleasonton's earlier work). If the electron-shakeoff process is also incorporated in the calculation, good agreement with experiment is achieved. Possible applications of the vacancy-cascade model are briefly discussed for other modes of inner-shell ionization and for molecular and solid-state systems. Probabilities of electron shakeoff from any shell of krypton are calculated for photo-ionization in the $1s$, $2s$, or $2p$ shell, for β^+ and β^- decay, and for Auger processes $1s$-$2p2p$, $2p$-$3p3p$, and $2p$-$3d3d$.

WHEN an atom is ionized in an inner shell it seems natural to describe the reorganization of the atom as a sequence of transitions, radiative and nonradiative, by which the original vacancy and those subsequently created by Auger events are transferred toward the outer shell in steps from shell to shell. If, indeed, reorganization is a stepwise process, each path will lead to a definite final-charge state, and the concert of all possible routes will result in a charge distribution. This description of the reorganization as a vacancy cascade was first proposed by Cooper,[1] and it was used thereafter to compute successfully charge distributions that result from electron capture[2] in ^{37}Ar, and from K photo-ionization[3] of argon. The model was also capable of making plausible multiple ionization of heavier elements following electron capture,[4] internal conversion[5] or ionization by x rays,[6] but it was not clear whether this simple scheme could account quantitatively for the observed charge distributions.

Krypton ionized in the K or L shell offers a good opportunity to apply the vacancy-cascade model to a more complex electronic configuration. Relative transition rates of both radiative and nonradiative processes are sufficiently well known for all series originating from any shell. Probabilities of electron shakeoff, which process was shown earlier[3,7–10] to accompany photoionization and Auger transitions, and *initial* vacancy distributions are also known under the excitation conditions that are of interest here. Values of these parameters entering into the model calculation are available from independent experiments or from theoretical predictions, most of which have proven reliable in different types of experiments.

In Sec. I we present the method of computing charge spectra and list individual charge distributions following the removal of a $1s$, $2s$, or $2p$ electron in krypton. In Sec. III we present experimental spectra that are the result of ejecting a K or an L electron by x rays. We compare then our calculated spectra with these experimental data and also with data collected earlier by Snell and Pleasonton for electron capture[4] in ^{79}Kr and β^- decay[11] in ^{85}Kr.

I. CALCULATION OF INDIVIDUAL CHARGE DISTRIBUTIONS

Three processes have been recognized as being active in the reorganization of the atom: radiative, Auger, and electron-shakeoff events. An inner-shell hole is filled by radiative transitions with the emission of a quantum or, alternatively, by Auger transitions with the emission of an electron. The process of electron shakeoff offers no additional way of filling a vacancy; it is rather a consequence of creating a vacancy. Electron shakeoff[12] may take place when the atomic

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

[1] E. P. Cooper, Phys. Rev. **61**, 1 (1942). Further justification comes from a recent experiment by H. W. Schnopper [Phys. Rev. **154**, 118 (1967)] which shows that the relaxation time of the atomic core is shorter than the lifetime of an inner shell vacancy.

[2] R. A. Rubenstein and J. N. Snyder, Phys. Rev. **99**, 189 (1955); A. H. Snell and F. Pleasonton, *ibid.* **100**, 1396 (1955).

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

[4] A. H. Snell, F. Pleasonton, and J. L. Need, Phys. Rev. **116**, 1548 (1959).

[5] F. Pleasonton and A. H. Snell, Proc. Royal Soc. (London) **A261**, 141 (1957).

[6] T. A. Carlson, W. E. Hunt, and M. O. Krause, Phys. Rev. **151**, 41 (1966). Individual charge spectra of krypton, cited here, are not based on a vacancy-cascade calculation, but were derived from the experimental distributions.

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

[8] M. O. Krause, T. A. Carlson, and R. Dismukes, Bull. Am. Phys. Soc. **11**, 353 (1966).

[9] M. O. Krause and T. A. Carlson, Bull. Am. Phys. Soc. **11**, 818 (1966).

[10] M. Wolfsberg and M. L. Perlman, Phys. Rev. **99**, 1833 (1955). At the present, we speak of shakeoff with an Auger process, when the Auger transition is between inner levels of the atom and the shakeoff electron comes from another higher shell; we speak of double Auger processes, when the two electrons come from the outer shell [T. A. Carlson and M. O. Krause, Phys. Rev. Letters **17**, 1079 (1966)].

[11] A. H. Snell and F. Pleasonton, Phys. Rev. **107**, 740 (1957).

[12] See, for example, E. L. Feinberg, J. Phys. (USSR) **5**, 423 (1941). As shown in Ref. 16 the energy of the photoelectron, for example, must be greater than about four times the energy of the electron considered for shakeoff, to fulfill the condition of suddenness.

field is changed sufficiently rapidly in terms of characteristic atomic times to cause excitation or ionization of orbital electrons. Therefore, nuclear β decay, where the process was first discovered, Auger transitions and many modes of initial ionization, as, i.e., photo-ionization, will be accompanied by shakeoff events.

In calculating charge distributions that follow inner-shell ionization, let us first restrict ourselves to the reorganization by radiative and Auger processes only: We trace all possible transition routes leading from the initial vacancy to the outer shell and note for each path the number of electrons lost in Auger events. Then we derive weighting factors for the routes from the (relative) rates of the individual transitions, which succeed each other within a route. We obtain the final charge distribution by grouping together paths that lead to the same charge states, and by considering the original charge state which may be -1, 0, or $+1$, depending upon the mode of excitation.

To introduce electron shakeoff, we distinguish between processes that are part of the reorganization and processes that are concomitant with the initial ionization act. Shakeoff accompanying Auger transitions is accounted for by simply adding routes parallel to Auger paths and weighting them by their probabilities of occurrence while reducing the transition rates of the "parent" Auger processes correspondingly. Shakeoff associated with initial ionization leaves the atom multiply ionized before reorganization starts. As a consequence, charge distributions need to be calculated for each combination of original vacancies, and superimposed according to the probabilities of creating holes in various shells. This method of including electron shakeoff becomes very cumbersome, when shakeoff of two and more electrons is also considered and when several consecutive processes are possible in a more complex atom. In such cases, we abandon the distinction between shakeoff with Auger and with initial ionization events and execute the computation in a simpler fashion, which takes advantage of the fact that shakeoff involves predominantly electrons in the outermost shells.[10,12] Suppose the probabilities of shaking off i electrons from the outer shell are P_{ij}, where $i=0$, 1, 2, $\cdots$, for a given process j, then the combined probabilities P_{iT} for a sequence of processes, for example, $j=1$, 2, 3, are given by

$$\begin{aligned} P_{0T}&=P_{01}P_{02}P_{03}, \\ P_{1T}&=P_{01}(P_{02}P_{13}+P_{03}P_{12})+P_{02}P_{03}P_{11}, \\ P_{2T}&=P_{01}(P_{03}P_{22}+P_{02}P_{23}+P_{12}P_{13}) \\ &\quad +P_{02}(P_{03}P_{21}+P_{11}P_{13})+P_{03}P_{11}P_{12}, \\ &\cdots \end{aligned} \tag{1}$$

Following the procedure outlined in the preceding paragraph, we calculate i charge spectra for electron configurations, which lack of i electrons, $i=0$, 1, 2, 3, in the outer shell in addition to the inner-shell vacancy, and superimpose these spectra according to the factors P_{iT} to arrive at the final distribution. If the reliability of transition rates and shakeoff probabilities warrants the effort, Eq. (1) can also be used to compute combined probabilities for shakeoff from other shells than the outer shell.

TABLE I. Relative transition rates (arbitrary units) for radiative and Auger transitions in krypton. Rates not listed are smaller than 0.5 units.

Initial state	Final state	Transition rate	Initial state	Final state	Transition rate
$1s$[a]	$2p$	58.0	$2p$[b]	$3p3p$	2.2
	$3p$	8.2		$3p3d$	4.6
	$4p$	0.8		$3d3d$	10.0
	$2s2s$	1.4		$3dN$	0.8
	$2s2p$	5.8			
	$2s3s$	0.6	$3s$[c]	$3p4p$	27.2
	$2s3p$	1.0		$3d3d$	18.1
	$2p2p$	17.3		$3dN$	51.6
	$2p3s$	1.0		NN	17.3
	$2p3p$	4.4			
	$3p3d$	0.5	$3p$[d]	$3d3d$	22
				$3dN$	23
$2s$[c]	$3p$	0.4		NN	5
	$2p3d$	49.6			
	$3s3s$	0.5	$3d$[d]	NN	69
	$3s3p$	2.6		NNN	31
	$3s3d$	1.1			
	$3p3d$	0.5			

[a] K-XY rates are those of bromine taken from P. Erman, I. Bergström, Y. Y. Chu, and G. T. Emery, Nucl. Phys. **62**, 401 (1965); ratios of dipole rates from A. H. Wapstra, C. J. Nijgh, and R. Van Lieshout, *Nuclear Spectroscopy Tables* (North-Holland Publishing Company, Amsterdam, 1959), p. 81; $\omega_K=0.66$ from J. Heintz, Z. Physik **143**, 153 (1955).
[b] M. O. Krause, Phys. Letters **19**, 14 (1966), and unpublished data.
[c] R. A. Rubenstein, thesis, University of Illinois, 1955 (unpublished).
[d] Reference 14.

To calculate individual charge distributions that follow the removal of a $1s$, $2s$, or $2p$ electron in krypton, we simulated the above scheme by a computer program. We employed a Monte Carlo technique, that is, the computer picks for each step possible transitions to a given vacancy or vacancies according to their relative rates, and notes the final number of vacancies, the charge distribution, after 10 000 cases have been computed. It uses the transition rates listed in Table I, which are those of radiative and Auger transition in a singly ionized atom, throughout the progression, regardless of the momentary hole configuration, but it changes the rates proportional to the number of electrons available to a particular transition. Keeping transition rates per electron constant ignores changes of transition rates due to changes of the atomic field whenever an additional inner-shell electron has been removed. This introduces only a slight error since Auger transition rates, by far the most likely events in the reorganization process, are usually rather insensitive to such changes.[13] Some exceptions, however, can be

[13] E. J. Callan, Phys. Rev. **124**, 793 (1961); W. N. Asaad, Nucl. Phys. **66**, 494 (1965). The Coulomb field of a krypton atom containing 2 $(3, 4\cdots,)$ inner-shell vacancies may be compared to the field of the elements Rb (Sr, Y, $\cdots$,). Coster-Kronig transition rates change more rapidly [E. J. Callan, Rev. Mod. Phys. **35**, 524 (1963)], but what is important here, the ratio of the Coster-Kronig transition to the Auger transitions remains almost constant, namely, about 0.9.

TABLE II. Probabilities (in percent) for electron shakeoff[a] from each shell in krypton due to photo-ionization and Auger processes. Initial hole or holes.

State vacated	1s	2s	2p	1s-2p2p	2p-3p3p	2p-3d3d
1s	0.004	0.000	0.000	0.003	...	...
2s	0.053	0.003	0.007	0.019	0.002	0.008
2p	0.27	0.026	0.034	0.016	0.032	0.03
3s	0.25	0.085	0.100	0.042	0.019	0.012
3p	1.22	0.523	0.59	0.22	0.05	0.067
3d	3.66	3.39	3.48	2.88	0.16	0.112
4s	2.23	1.85	1.98	1.46	0.95	1.00
4p	13.90	12.18	12.37	7.23	5.09	5.36
Total	21.6	18.1	18.6	11.9	6.30	6.59

[a] Includes excitation into unoccupied bound levels; excitation is, however, a rare event compared to ionization (Refs. 8, 10, and 15).

found, especially in the regime of Coster-Kronig transitions. In the present calculation we encountered two cases, the transitions $3p$-$3d3d$ and $3d$-NNN, which become energetically forbidden when certain electrons were previously removed.[14] Since the program did not provide for this complication, an adjustment was made following the computer printout.

We incorporated electron shakeoff into our scheme by removing from the program a $3p$, $3d$, or up to two N electrons in addition to the $1s$, $2s$, or $2p$ electron, *before* the vacancy cascade started. The weighting factor for the resulting spectra were gained from the expressions (1) using the calculated shakeoff probabilities listed in Table II for initial ionization events and the most frequent routes of reorganization. We neglected shakeoff from deeper lying shells and simultaneous shakeoff from two different shells, such as $3d$ and N.

The values listed in Table II were obtained from the equation

$$P_{n,l}=1-\left[\left|\int \psi_{f,nl}{}^{*}\psi_{i,nl}d\tau\right|^{2}\right]^{N}-NP_{F}, \qquad (2)$$

which follows[3,12,15] from the sudden (nonadiabatic) perturbation theory, where $\psi_{i,nl}$ and $\psi_{f,nl}$ represent Hartree-Fock wave function of an electron with the quantum numbers n, l before and after the emission of an inner-shell electron; N is the number of like electrons and NP_F is the probability of transitions to levels forbidden by the Pauli principle. In Table III we present, as a typical example, numerical values of shakeoff probabilities appropriate to the sudden creation of a $2s$ vacancy and subsequent atomic readjustment by the most probable route. We see that electrons are shaken off in about 25% of the events from the N shell and in about 4% of the events from inner shells. Similar values are obtained for a sudden[12] $1s$ vacancy and slightly lower values for a sudden $2p$ vacancy, while electron loss by shakeoff following the slow (adiabatic) production of a hole in these levels occurs in less than 15% of the cases.

[14] M. O. Krause and T. A. Carlson, Phys. Rev. **149**, 52 (1966).
[15] C. W. Nestor, T. C. Tucker, T. A. Carlson, L. D. Roberts, F. B. Malik, and C. Froese, Oak Ridge National Laboratory Report No. ORNL 4027 (1966) (unpublished); this report can be obtained from the authors.

TABLE III. Calculated probabilities[a] of losing zero to three electrons from the N shell of krypton by shakeoff associated with the processes: (1) photo-ionization in $2s$ shell, (2) Auger transition[b] $2s$-$2p3d$, and (3) Auger transition $2p$-$3d3d$. Also given are the probability P_{0j}' of losing no electron from any shell and the combined probabilities P_{iT} according to Eq. (1) for the successive occurrence of the events (1), (2), and (3). Values are in percent. The first index of the symbols P_{ij} designates the number of electrons lost, the second index denotes the process.

Process/hole(s)	P_{0j}'	P_{0j}	P_{1j}	P_{2j}	P_{3j}	P_{Nj}
(1) $2s$	81.9	86.0	13.0	1.0	0.05	14.0
(2) $2s$-$2p3d$	93.5	93.5	6.3	0.2	...	6.5
(3) $2p$-$3d3d$	93.4	93.6	6.2	0.2	...	6.4
P_{0T}' and P_{iT} (i=0,1,2,3,N)	71.4	75.3	21.5	3.1	0.1	24.7

[a] Values of P_{0j}' and P_{Nj} are taken from Table II; multiple shakeoff is deduced from the approximate expressions $P_{2j}=\frac{1}{2}P_{Nj}{}^{2}$ and $P_{3j}=\frac{1}{6}P_{Nj}{}^{3}$. Definitions: $P_{0j}=1-P_{Nj}$; $P_{0T}=1-P_{NT}$; $P_{Nj}=\sum_i P_{ij}$, and $P_{NT}=\sum_j P_{jT}$, with $i=1, 2, 3$.
[b] Probabilities for this transition were not calculated, but estimated from the values for the transitions $2p$-$3d3d$ and $2p$-$3p3p$.

We display the results of our calculation in three sets. In Table IV, set A shows the extent of ionization for the hypothetical case of having only radiative and Auger transition participate in the readjustment to a vacancy formed adiabatically; set B corresponds to the slow production of the initial vacancy and reorganization by radiative, Auger, and shakeoff processes, while set C corresponds to reorganization following a sudden initial ionization event as encountered in the photo-ionization processes dealt with in this paper. To check the validity of our model by comparison with experimental data we need to superimpose these individual charge spectra

TABLE IV. Individual charge distributions (in percent) of krypton ions following creation of a $1s$, $2s$, or $2p$ vacancy. Calculation according to a vacancy-cascade model in which the following parameters enter: set A: Auger and radiative transitions. set B: Auger and radiative transitions, and electron shakeoff associated with Auger processes. set C: Auger and radiative transitions, and electron shakeoff associated with both Auger processes and initial inner-shell ionization.

	Set A			Set B			Set C		
Charge	1s	2s	2p	1s	2s	2p	1s	2s	2p
1	0.8	0.4	0	0.7	0.3	0	0.6	0.3	0
2	1.5	0.1	1.4	1.4	0.1	1.3	1.2	0.1	1.0
3	6.9	0.6	3.6	6.2	0.5	3.5	5.2	0.4	3.0
4	26.1	1.3	41.1	23.6	1.2	38.6	20.1	0.9	31.8
5	20.3	6.0	34.3	21.3	5.4	35.5	21.7	4.8	36.9
6	9.9	40.6	15.2	11.0	36.1	16.1	12.7	29.8	18.3
7	6.7	38.1	4.3	7.2	39.4	4.9	8.6	39.5	7.5
8	14.5	12.8	0.1	14.1	16.5	0.1	13.6	21.8	1.4
9	9.5	0.1		9.9	0.5		10.6	1.9	0.15
10	3.2			3.7	0.1		4.5	0.5	
11	0.6			0.8			1.1		
12	0.06			0.1			0.15		
13							0.02		
Mean charge	5.78	6.51	4.72	5.88	6.64	4.77	6.07	6.81	4.98

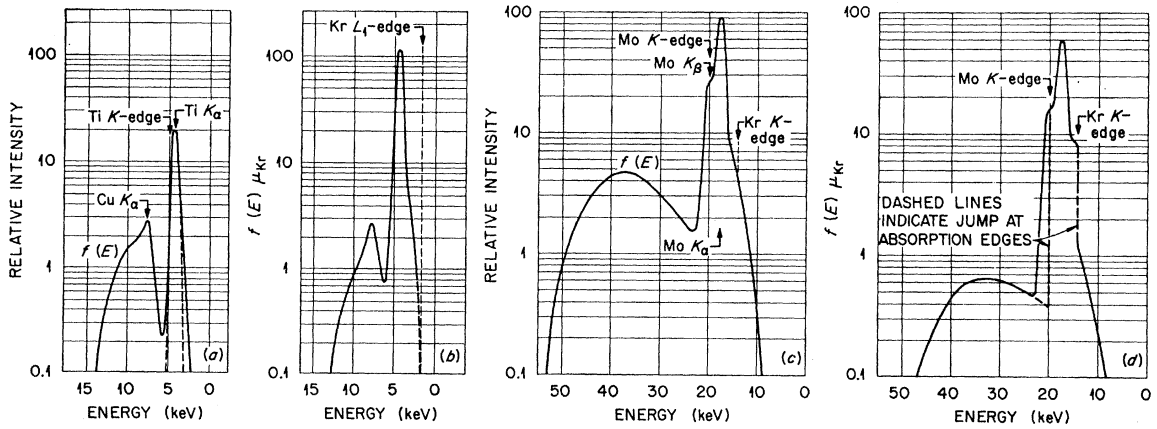

FIG. 1. Energy spectra of x rays used to produce vacancies in the L shell (a) and in the K shell (c) of krypton. Figures (b) and (d) indicate relative number of vacancies produced by x rays of energy E from the distributions $f(E)$. X rays from the Ti anode were filtered through 11 mg/cm² Ti and 52 mg/cm² Be, x rays from Mo target through 50 mg/cm² Mo, 35 mg/cm² Al, and 240 mg/cm² Be. Ordinates in arbitrary units; μ_{Kr} is the photoabsorption coefficient of krypton.

according to actual initial vacancy distributions that are created in the interaction of electromagnetic fields or particles with orbital electrons. The results are given in Sec. III.

To arrive at an estimate of the accuracy of the charge distributions summarized in Table IV, we varied the more important transition rates and shakeoff probabilities (see Tables I and II) within their reported or estimated error limits in such a way as to achieve maximum distortion of the spectra. The following errors that entered the calculation are reported in terms of $\sigma_{\pm}$ (approximate values): $1s$–XY Auger rates, 10%; ω_K which established the ratio of radiative to Auger transitions, 5%; $2p$-XY rates, 10%; $3p$-XY rates, 25%; $3d$-$NN(N)$ rates, 15%. The error of the significant ratio $2s$-$2p3d/2s$-XY should not exceed 5%; whereas the $3s$-XY rates, which are of minor importance in this study, may be in error by as much as 30%. For shakeoff of M and N electrons in the process of photoabsorption we estimate the accuracy of the probability values to be 5–10% on the grounds that our calculated values appropriate to photo-ionization of neon and argon compare to this extent with experimental data.[8,9] An error of 50% should, conservatively, be assigned to the probabilities calculated for shakeoff with Auger processes and for multiple events. Thus, P_{1T}, P_{2T}, and P_{3T} values as given in Table III should be multiplied by 1.25, 1.7, and 5, respectively, to obtain, for example, the upper bounds. We conclude from the results of our approximate error analysis that the relative intensities of the more probable ion charges of the $2s$ spectra are certain to about ±20% for set A and to about ±25% for sets B and C. Intensities of charge states that are produced via less frequent routes are often less accurate, because low transition rates are not as well known as the high rates. The $2p$ spectra are somewhat more accurate than the $2s$ spectra and the $1s$ spectra are slightly less accurate. The assumption of the invariance of transition rates during the readjustment process should not introduce any significant additional error.

II. EXPERIMENTAL

Apparatus and experimental procedure were the same as in previous experiments.[3,14,16] X rays from a Mo tube were chosen to produce vacancies primarily in the K shell of krypton and x rays from a Ti anode to produce vacancies primarily in the L shell. Proximity of the characteristic lines to either the K or the L edge of krypton and selective filtering of the emitted x rays assured that most of the vacancies were formed by K series lines of Mo and Ti, respectively, and by continuum x rays of nearly the same energies as these lines. Measurements with a proportional counter verify

TABLE V. Comparison of experimental and calculated charge spectra following photo-ionization primarily in the L shell of krypton. I=Auger and radiative processes only. II=Electron shakeoff included. Abundances are in percent.

	Experiment		Cascade model		Ratio (theory II/expt)
Charge	Observed	Pressure-corrected	I	II	
1	1.9	1.3±0.6	0.4	0.4	0.31
2	3.6	3.3±0.6	3.2	2.7	0.82
3	7.6	7.3±0.6	8.3	7.3	1.00
4	21.4	20.9±0.9	28.2	22.7	1.09
5	23.3	23.3±0.9	21.4	23.4	1.00
6	22.0	22.5±1.1	20.8	19.4	0.86
7	14.7	15.2±0.8	13.8	15.9	1.05
8	4.6	5.0±0.5	3.8	7.3	1.46
9	0.8	1.0±0.3	0.03	0.7	0.70
10	(0.1)[a]	(0.2)[a]	···	0.15	(0.8)
Mean charge	5.14	5.22	5.04	5.29	1.01

[a] Evaluated from run without Ti filter.

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

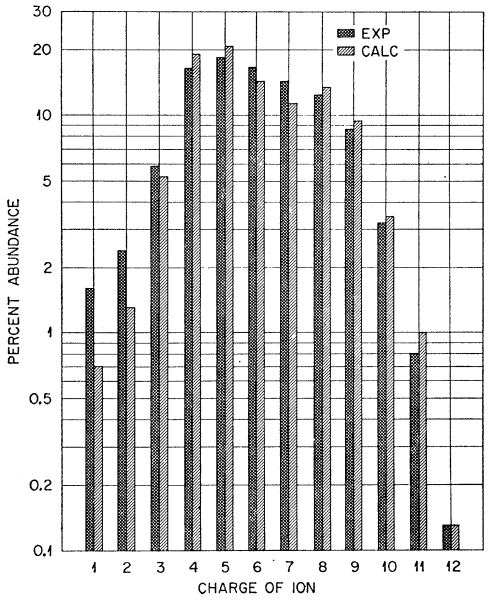

FIG. 2. Experimental charge distribution resulting from irradiation of krypton by Mo K x rays compared with calculated spectrum. About 90% of the primary vacancies are produced in the K shell.

this, as seen from Fig. 1, where fully corrected x-ray distributions are displayed together with curves which indicate, on a relative scale, how many vacancies were due to x rays of a given energy. Ions formed by the reorganization of the atom were magnetically analyzed and detected in the counting mode by an openface electron multiplier. Gas pressure in the source volume ranged from 1 to 2.5×10^{-5} Torr for various runs, and it was about 5 times lower in the analyzer section. At these pressures, charge-transfer reactions were infrequent, so that only small corrections had to be applied to the observed abundances of ions. Each of the spectra reported represents an average from at least three separate runs. Errors quoted are largely statistical except for charge 1. Here the error was increased because of an uncertain contribution to ionization by stray electrons.

III. COMPARISON OF EXPERIMENTAL RESULTS WITH CALCULATED CHARGE SPECTRA

A. Photo-Ionization in the L shell

In Table V experimental charge distributions, arising from photo-ionization in the L shell, and to a lesser extent in the M shell, are compared with calculated spectra that are the result of the stepwise reorganization of the atom. In column 2 we present the observed charge distribution and in column 3 the pressure corrected spectrum. Two calculated spectra are listed; spectrum I ignores shakeoff entirely, spectrum II allows for shakeoff as a concomitant to Auger transitions and initial ionization. The spectra were obtained by weighting the entries of set A (spectrum I) or set C (spectrum II),

TABLE VI. Comparison of experimental and calculated charge spectra resulting from photo-ionization primarily in the K shell of krypton. Calculation with (II) and without (I) electron shakeoff. Relative abundances are in percent.

Charge	Experiment	Cascade model I	Cascade model II	Ratio (theory II/expt)
1	1.6 ±0.5	0.9	0.7	0.44
2	2.4 ±0.4	1.5	1.3	0.54
3	5.8 ±0.5	6.7	5.1	0.88
4	16.2 ±0.5	24.6	19.0	1.17
5	18.1 ±0.5	19.5	20.6	1.14
6	16.5 ±0.7	12.6	14.2	0.86
7	14.1 ±0.6	9.2	11.1	0.79
8	12.4 ±0.6	13.6	13.6	1.10
9	8.6 ±0.7	8.2	9.4	1.09
10	3.4 ±0.5	2.7	3.9	1.15
11	0.8 ±0.2	0.5	1.0	1.25
12	0.13±0.10	0.05	0.13	1.00
13	...	...	0.02	...
Mean charge	6.00	5.76	6.06	1.01

and those of Table IV in Ref. 14 according to the following initial vacancy distribution: $2s=0.30$; $2p=0.563$; $3s=0.05$; $3p=0.07$; $3d=0.015$; and $N=0.003$. This initial vacancy distribution corresponds to the relative photoabsorption of x rays from a Ti anode, Fig. 1(b), in the various subshells of krypton, and it is almost the same distribution that would be produced by monochromatic TiK_α x rays. We relied on a modified Stobbe-Hall formula[17] to determine the absorption in the $2s$, $2p$, and M levels, but instead of splitting M-shell absorption into $3s=0.043$, $3p=0.089$, and $3d=0.003$ according to this formula we preferred to estimate these coefficients by extrapolating earlier data.[14] We also estimated N-shell absorption and included ionization by Compton scattering.

In the present case, as well as in the case of photo-ionization in the K shell, Sec. III.B, the use of set C is justified by the fact that the majority of the x rays produce photoelectrons fast enough to fulfill the condition[12] of suddenness, regarding M and N electrons. The accuracy of the calculated spectra, listed in Tables V and VI, is as good as the accuracy of the individual distributions, since the x-ray spectra of Fig. 1 and the partial photoabsorption coefficients for $1s$, $2s$, and $2p$ electrons are considered to be very reliable, whereas the less dependable coefficients for N and M electrons have only a small influence on the relative intensities of ion charges.

We see from Table V that the vacancy-cascade model which incorporates radiative, Auger, and shakeoff processes is capable of accounting satisfactorily for the experimental charge distribution. Auger events are responsible for the bulk of ionization and the general shape of the distribution; electron shakeoff smoothes the spectrum out and shifts it toward the higher charge end.

[17] A. J. Bearden, J. Appl. Phys. **37**, 1681 (1966); A. J. Bearden, University of California, San Diego, Report, 1965 (unpublished).

TABLE VII. Experimental and calculated charge spectra resulting from electron capture and β decay of krypton. Abundances are in percent.

	Electron capture		β^- decay		β^+ decay[c]
Charge	Expt[a]	Calc	Expt[b]	Calc	Calc
−1	...	...	...	...	68.6
0	(0.7)[d]	0.7	...	...	20.8
+1	1.8	1.3	79.2	77.3	5.3
2	4.7	5.8	10.9	13.9	2.9
3	14.4	20.2	3.91	3.77	1.4
4	18.8	18.4	3.12	3.14	0.5
5	16.7	13.1	1.51	1.15	0.3
6	15.8	10.6	0.66	0.39	0.14
7	13.2	15.6	0.40	0.17	0.06
8	9.9	9.8	0.19	0.11	0.01
9	3.9	3.6	0.093	0.056	...
10	0.79	0.9	0.026	0.011	...
11	0.16	0.09	<0.003	0.002	...
12	0.06	0.01	...	...	...
Mean charge	5.25	5.11	1.42	1.40	−0.48

[a] Reference 4.
[b] Reference 11.
[c] In calculating this spectrum we have assumed that 85% of the N shakeoff electrons go into the continuum and 15% into excited states.
[d] Inferred.

B. Photo-Ionization in the K Shell

Vacancies produced by x rays of energies near 17.5 keV give rise to the charge distribution listed in Table VI. Again, two calculated spectra are given, showing the extent of ionization that follows from the cascade model with and without electron shakeoff. The calculation is based on the following initial vacancy distribution: $1s=0.865$, $2s=0.083$, $2p=0.037$, $3s=0.007$, $3p=0.004$, $3d=0.002$, and $N=0.002$. These values were obtained in the same manner as those for L ionization.

Agreement between experiment and the calculated spectrum that includes electron shakeoff is satisfactory, as can also be seen from the histogram of Fig. 2. Overestimate of the intensity of Kr^{4+} and underestimate of the intensity of Kr^{7+}, both of which are more pronounced in the charge spectrum due to electron capture[18] (see below), may be due to one or a combination of the following factors: (a) shakeoff probabilities for Auger processes L-MM are greater than calculated, (b) shakeoff accompanying M-NN transitions cannot be neglected, and (c) multiple shakeoff probabilities are greater than estimated. A small change in these parameters could improve the K spectra without, at the same time, impairing the L spectrum listed in Table V.

C. Electron Capture $^{79}Kr \rightarrow {}^{79}Br$

We test our calculation against a third experimental charge distribution, reported by Snell *et al.*[4] for the decay of ^{79}Kr. Results are summarized in Table VII. The experimental data[4] were corrected for the β^+ branch of the decay with the aid of the charge spectrum listed in column 6, which is based on the following calculated shakeoff probabilities for β^+ decay (in percent): $1s=0.074$, $2s=0.20$, $2p=0.42$, $3s=0.53$, $3p=1.70$, $3d=3.73$, $4s=10.0$, $4p=19.8$. We used in the calculation the following vacancy distribution appropriate to electron capture: $1s=0.90$, $2s=0.09$, $3s=0.01$. We neglected, however, the creation of additional vacancies in the K and L shells by internal conversion, which accompanies electron capture in less than 1% of the events. Since we are dealing with a bromine atom, we changed the fluorescence yield ω_K accordingly but retained the remaining rates of Table I. As a consequence, the $1s$ charge distribution of Table IV, set B, is slightly shifted toward the higher charges, whereas the other spectra remain unchanged. Shakeoff associated with the initial hole production, being negligibly small, was not considered.[15] Agreement between calculated and experimental spectra is fair; discrepancies appear in the same places as for photoionization.[18] The similarity of the experimental distributions following electron capture and x irradiation is striking. Evidently the absence of shakeoff in the process of electron capture is well compensated by the creation of a larger number of holes in the deeper lying shells and production of additional holes by internal conversion.

D. β^- Decay $^{85}Kr \rightarrow {}^{85}Rb$

Again referring to Snell and Pleasonton,[11] we compare their data with our calculation, Table VII. Although this case is rather a test of our computed shakeoff probabilities and our handling of multiple shakeoff, it still affords an opportunity to apply the cascade model to account for the general profile of the distribution and particularly for the occurrence of the higher charge states. We note that here the initial vacancies are formed by the shakeoff process associated with β decay. The following percent probabilities P_x of electron shakeoff were calculated[17,19] with the aid of Eq. (2): $1s=0.07$ $2s=0.174$, $2p=0.324$, $3s=0.460$, $3p=1.41$, $3d=3.39$, $4s=2.83$, $4p=14.1$. Probabilities of multiple electron shakeoff were derived from the approximate expressions: $\frac{1}{2}P_{4p}{}^2$, $\frac{1}{6}P_{4p}{}^3$, $P_{3d}\cdot P_{4p}$, etc., where the P_x stand for the shakeoff probabilities given above. With these values of single and multiple shakeoff,[19a] representative of the fractional number of vacancies formed per β decay, we weighted the spectra of set B, Table IV, and those of Table IV in Ref. 14. The resulting spectrum is in satisfactory agreement with the experimental distribution. It underestimates, however, the intensities of the highly charged species to a similar extent as found earlier for the β decay in neon.[20]

[18] Charge states produced by electron capture should be shifted by +1 unit to allow comparison with those arising from photoionization.

[19] An earlier calculation by A. E. S. Green, Phys. Rev. **107**, 1646 (1957) yields lower values because of less accurate wave functions.

[19a] *Note added in proof.* See footnote (a) of Table III for definitions.

[20] T. A. Carlson, Phys. Rev. **130**, 2361 (1963).

Since in the β decay of ^{23}Ne no vacancy cascade needed to be invoked, we suspect that our estimates of multiple shakeoff have been too low in either case.

The differences between experimental and calculated intensities of Kr^{1+} and Kr^{2+} are small but significant for the following reason: Our shakeoff calculations give the probability of removing an electron from its orbital without specifying whether it is promoted to a higher bound state or to the continuum. In the previous cases, this has been of little consequence, since electron excitation by shakeoff occurred simultaneously with the creation of inner-shell vacancies, thereby resulting in a high probability of auto-ionization of the excited electron. In the present case, an analogous consideration applies to the excitation of an inner electron, but any $4s$ or $4p$ electron excited into an optical level will remain bound and will not alter the original charge state of the atom. From previous data[7] and recent measurements[8,9] we know that excitation occurs in about 10% of the events as compared to 90% for ionization. Adjusting the intensities of Kr^{1+} and Kr^{2+} by this factor leads, indeed, to a better agreement in charge states one and two.

E. Other Modes of Ionization

When inner-shell ionization is not as probable as outer-shell ionization, as for electron bombardment,[21] or when inner-shell ionization is frequently accompanied by outer-shell ionization, as for atomic collisions,[22] multiply charged species are only partially due to a vacancy cascade induced by an inner-shell vacancy. By calculating probabilities of inner-shell relative to outer-shell ionization from theory or by measuring their frequency of occurrence (looking at quanta or Auger electrons of the first step of the cascade), one may then with the aid of the vacancy-cascade model determine the contributions of inner-shell vacancies to the observed charge distribution. This would, doubtless, help our understanding of multiple outer-shell ionization by electrons and atomic particles.

When an atom with an inner-shell vacancy is incorporated in a molecule or lattice, the vacancy cascade will proceed as if it were in an isolated atom, though the environment may be felt in the last step to the valence electrons or band. Lifetime and fate of the highly charged ion and its effects on the surroundings will largely depend on properties of the medium in question. Platzman[23] and Varley[24] have discussed some of the aspects for the solid phase; Wexler *et al.*,[25] Snell and Pleasonton,[26] and, in particular, Carlson and White[27] have presented data which exhibit in a spectacular manner the destructive impact of a vacancy cascade on gas molecules. These experiments demonstrate that, contrary to Cooper's prediction,[1] constituent atoms of the molecule will not have separated appreciably in the time required for the vacancy cascade to reach the outer levels. Thus, in times of about 10^{-15} sec a high positive charge can be accumulated and spread over the molecule, causing a violent breakup by Coulombic forces.

IV. CONCLUSIONS

We have treated the reorganization of a krypton atom with an inner-shell vacancy as a vacancy-cascade process in which the original vacancy and subsquently created vacancies are transferred toward the outer shell in steps from shell to shell. We have regarded radiative, Auger, and electron shakeoff processes as individual processes participating in the atomic reorganization. With this approach we have been able to account quantitatively for experimental charge distributions that arise from such different modes of initial ionization as photoionization, electron capture, and β decay. Agreement between our calculation and the experiments quoted in this paper as well as those presented earlier for the simpler cases of initial ionization in the K shell of argon and M shell of krypton suggests that the vacancy-cascade model offers an adequate description of the reorganization regardless of element and location of the original vacancy. As a consequence of this way of electronic rearrangement, the positive energy of an inner-shell ionized atom is expended largely by quanta and Auger electrons in discrete amounts and, to a lesser extent, by low-energy shakeoff electrons in a continuous distribution.

ACKNOWLEDGMENTS

We greatly appreciate the valuable help of C. W. Nestor, who computed for us wave functions and overlap integrals pertaining to electron shakeoff. We are indebted to D. E. Arnurius for setting up the Monte Carlo program.

[21] F. Fiquet-Fayard, J. Chim. Phys. **59**, 439 (1962); J. P. Ziesel, *ibid.* **62**, 328 (1965); B. L. Schram, Physica **32**, 197 (1966).

[22] See, for example, E. Everhart and Q. C. Kessel, Phys. Rev. **146**, 27 (1966); L. I. Pivovar, M. T. Novikov, and A. S. Dolgov, Zh. Eksperim. i Teor. Fiz. **49**, 734 (1965) [English transl.: Soviet Phys.—JETP **22**, 508 (1965)].

[23] R. L. Platzman, *Symposium on Radiobiology*, edited by J. J. Nickson (John Wiley & Sons, Inc., New York, 1952).

[24] J. H. O. Varley, Nature **174**, 886 (1954).

[25] S. Wexler and G. R. Anderson, J. Chem. Phys. **33**, 850 (1960); S. Wexler, in *Actions Chimiques et Biologiques des Radiations*, edited by M. Haissinsky (Masson & Cie, Paris, 1965), 8th series.

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

[27] T. A. Carlson and R. M. White, J. Chem. Phys. **44**, 4510 (1966).