PHYSICAL REVIEW VOLUME 151, NUMBER 1 4 NOVEMBER 1966

Relative Abundances of Ions Formed as the Result of Inner-Shell Vacancies in Atoms*

THOMAS A. CARLSON, W. E. HUNT,† AND MANFRED O. KRAUSE
Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received 2 June 1966)

Relative abundances of differently charged ions were measured following the **x irradiation** of Xe, and, in separate experiments, of Hg. These studies were carried out for a variety of x-ray energies in order to obtain data as a function of the initial inner-shell vacancies. From the data we have derived charge spectra that result from producing an initial vacancy in each of the following shells: the K, L_{I}, $L_{\mathrm{II,III}}$, M_{I}, $M_{\mathrm{II,III}}$, $M_{\mathrm{IV,V}}$, and N shells of Xe; and the L, M, N, and O shells of Hg. These data are correlated with earlier measurements on He, Ne, Ar, and Kr; and empirical rules are set up whereby one may estimate the average charge resulting from the atomic readjustment to a vacancy in any shell of any atom.

I. INTRODUCTION

WHEN a vacancy is created in the inner shell of an atom, it may be filled by either a radiative transition or an Auger process. New vacancies created in this transition may in turn be filled by further transitions, and this continues until all vacancies reach the outermost occupied shell. With the exception of the K and L shells of the heavy atoms, Auger processes are much more probable than radiative transitions, and since an electron is ejected in each Auger process, a series of such events, called a vacancy cascade, gives rise to a highly charged ion.

The formation of an inner-shell vacancy is a common event in nature, taking place, for example, in x irradiation by way of photoelectron emission, or when such nuclear events as electron capture or internal conversion occur. We have undertaken a systematic study[1–4] of the atomic readjustment to an inner-shell vacancy by measuring in a specially designed mass spectrometer the relative abundances of differently charged ions that are the result of irradiating atomic gases with x rays. One of the reasons for this study has been the desire for a better understanding of the basic processes leading to multiple ionization. Another purpose of the investigations is simply the knowledge of the extent of ionization that occurs as the result of forming a hole in a given shell of an atom. These data should be useful, for example, to those involved in studies of radiation damage and radiation detectors.

In this paper we present data on the charge spectra of Hg and Xe measured as a function of the x-ray energy. From these data we can estimate the charge spectrum associated with the formation of a vacancy in the K, L, M, and N shells of Xe, and the L, M, N, and O shells of Hg. We have then correlated these analyses with previous work on the lighter rare gases and have derived a recipe and a plot to enable the reader to estimate the average charge for the atomic readjustment to a vacancy in any shell of any atom in the periodic table.

II. EXPERIMENTAL

The atomic gas to be studied is allowed to leak into our charge spectrometer, where it is irradiated with x rays. The differently charged ions that are formed are collected and analyzed for their relative abundances by means of a magnetic analyzer. The spectrometer and the experimental procedures used in our studies have been described before.[2] As was done in previous studies, precautions were taken against ion-gas collisions that may distort the spectra at higher pressure, and against ionization from secondary electrons. Since the vacancy cascade takes place in the order of 10^{-15} sec, and the time for collecting and analyzing the ions is about 10^{-5} sec, one observes the final ionization states that have been the result of atomic readjustments to inner shell vacancies.

It is desirable to use a monochromatic source of x rays. The use of a crystal monochromator has been ruled out at this time, because the loss of x-ray intensities encountered with such an instrument is too costly. However, by the proper choice of targets, the operating voltage of the x-ray tube, and filters, it has been usually possible to produce the initial vacancy primarily with one characteristic x-ray line, or at least with x-rays of energies close to this line. The validity of this statement, based in part on measurements of x-ray spectra, has been discussed earlier.[2,4] X-ray sources used for the Xe and Hg studies are given in Table I. In discussing our results, we shall take as the x-ray energy the values given in the last column. These energies normally correspond to the most prominent characteristic line. In the case of the x-ray sources, I and J, we have used the average energy that gives rise to photo-ionization, as estimated from Kulenkampff's formula[5] for the shape of bremsstrahlung, the photo-

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

† Present address: David Lipscomb College, Nashville, Tennessee.

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

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

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

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

[5] H. Kulenkampff, Ann. Physik **69**, 548 (1921); H. Kulenkampff and L. Schmidt, *ibid.* 43, 494 (1943).

TABLE I. Summary of x-ray sources used in the x irradiation of Xe and Hg.

X-ray source	Type of tube[a]	$E_{\max}$[b]	Target	Filter [mg/cm²]	E[c]
A	1	52	Mo	52Mo+34Al+230Be	K_α 17.5
B	1	31	W	18Zn+51Be	L_α 8.4
C	2	11	V	11Ti+9Be	K_α 4.96
D	1	20	Ti	11Ti+51Be	K_α 4.5
E	2	4.2	Al	3.5 Al	K_α 1.5
F	2	3.0	Al	2.1 Al	K_α 1.5
G	2	2.0	Zn	1.3Zn+0.11 polystyrene	L_α 1.014
H	2	2.0	Ni	0.45 Ni	L_α 0.853
I	2	0.65	W	0.45 polystyrene	$\bar{E}$ 0.240
J	2	0.35	W	0.25 polystyrene	$\bar{E}$ 0.215

[a] No. 1 designates a Machlett AEG-50 x-ray tube; No. 2 designates a tube designed by J. A. Bearden and described in Ref. 2.

[b] Maximum energy of the electrons striking the target in keV.

[c] Designation and energy in keV of most prominent characteristic line except for symbol $\bar{E}$ which indicates average energy of x ray weighted by the photoelectric cross section of the element under investigation.

electric cross section[6] of Xe and Hg, and the absorption of the polystyrene filter.[7]

III. EXPERIMENTAL RESULTS FOR Hg AND Xe

The relative abundances of the differently charged ions that are the result of the x irradiation of Hg and of Xe are shown in Table II for a variety of x-ray sources. The quoted uncertainties are taken from counting statistics, except for charge-one, which includes a correction for secondary ionization.

For a comprehensive picture of the effects of producing innershell vacancies, we can add to the present data on Hg and Xe, the earlier work in which vacancies were produced primarily in the K shell[1,4] of Ne, the K and L shells[2] of Ar, the K and L shells[8] of Kr, and the M shell[9] of Kr. In addition there are results on the outer shells[10] of He, Ne, and Ar. Besides our studies using x rays, there have been those on atoms undergoing radioactive decay by means of electron capture and internal conversion. In these investigations the initial atomic vacancy was formed primarily in the K shell[11] of Xe, the K shell[12] of Cl, and the L shell[13] of Th.

IV. ANALYSIS OF DATA

Photoabsorption can take place in any shell whose binding energy is less than the x-ray energy. However, the cross section for a x ray is usually dominated by one or two shells; and, in general, the greatest relative absorption is for the shell whose energy is closest that of the x ray. By the proper choice of x-ray energy one can produce vacancies primarily in one of the different shells of an atom. The experimental spectrum S_e is made up of contributions from each of the individual shells weighted by a_{nl}, viz.:

$$S_e=\sum_{nl} a_{nl}S_{nl}. \tag{1}$$

S_{nl} is the charge spectrum associated with the shell nl, where n is the principal and l the angular-momentum quantum number. The spectra in Eq. (1) are normalized to a total abundance of 1.0, and $\sum a_{nl}=1.0$. Addition of spectra and multiplication by a constant imply

$$S(I_1,I_2\cdots)+S(I_1',I_2'\cdots)=S(I_1+I_1',\,I_2+I_2'\cdots)$$

and

$$aS(I_1,I_2\cdots)=S(aI_1,aI_2\cdots)\,,$$

where I_n and I_n' are the relative abundances of charge n for the different spectra. In Eq. (1) we have not considered j-j coupling, which in the heavier elements leads to a splitting of the energy levels[14] that is sufficiently large to allow for Coster-Kronig transitions; e.g., in Xe we can have the transition L_{II}-$L_{\mathrm{III}}M$. However, experimental evidence[15] indicates that such transitions are usually not dominant in the filling of a vacancy in the lower j state, so that one would not expect a large difference in the charge spectra arising from vacancies in the two levels. A more detailed investigation of this problem in the future, however, would be desirable.

The spectra, obtained for the individual shells by solving a set of simultaneous equations of the type given by Eq. (1), can be generally construed as those relating to the *sudden* production of a vacancy, regardless of the mechanism for producing the vacancy, although there may be extenuating circumstances that could alter the extent of ionization. (For example, in electron capture there is also a change in the nuclear charge.) We have stressed the term "sudden," since in most studies an electron vacates its state with a velocity large compared to the velocities of the outer electrons. In this situation electron shakeoff may take place as the result of a sudden change in the effective charge and is independent of the velocity of the outgoing electron. Since electron shakeoff is most probable for the electrons in the outer shell, the criteria of "suddenness" is met (for practical purposes) unless the energy of the outgoing electron is near the ionization threshold of the outermost shell. (For an experimental evaluation of electron shakeoff as a function of the photoelectron energy, see Ref. 4.)

To obtain the proper values of a_{nl} in Eq. (1), we need

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[6] A. H. Compton and S. K. Allison, *X Rays in Theory and Experiment* (D. Van Nostrand Company, Inc., New York, 1935), pp. 800–806.

[7] Based on cross section for carbon as obtained from Ref. 6 and Jönsson's rule for the K absorption jump [A. H. Compton and S. K. Allison, Ref. 6, p. 537].

[8] M. O. Krause and T. A. Carlson (to be published); see also Bull. Am. Phys. Soc. **9**, 51 (1964).

[9] M. O. Krause and T. A. Carlson, Phys. Rev. **149**, 52 (1966).

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

[11] F. Pleasonton and A. H. Snell, Proc. Roy. Soc. (London) **241A**, 141 (1957).

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

[13] K. Gunter, F. Asaro, and H. C. Helmholz, Phys. Rev. Letters **16**, 362 (1966).

[14] Designated by $p_{1/2}$ and $p_{3/2}$; $d_{3/2}$ and $d_{5/2}$; $f_{5/2}$ and $f_{7/2}$, which in x-ray terminology are given by II, III; IV, V; and VI, VII.

[15] L_{II}-L_{III} M transitions are energetically possible only for the elements $Z=22$ to 30 and for $Z>90$, while measurements on L_{II}-$L_{\mathrm{III}}N$ transitions show that these transitions, although not negligible, are not dominant. For example, see P. V. Rao and B. Crasemann, Phys. Rev. **139**, A1926 (1965).

TABLE II. Percent abundances of ions formed in the x irradiation of Xe and Hg for various x-ray sources.

			Run[a]		
Charge	Hg*L* (*A*)	Xe*L* (*B*)	Xe*L* (*C*)	Hg*M* (*D*)	Xe*M* (*E*)
1	1.0±0.4	0.8 ±0.4	0.9 ±0.5	0.8 ±0.5	1.5 ±0.5
2	1.9±0.4	1.4 ±0.2	1.8 ±0.2	3.2 ±0.3	5.8 ±0.3
3	2.7±0.5	1.9 ±0.1	3.6 ±0.4	3.9 ±0.3	6.4 ±0.3
4	5.0±0.6	5.4 ±0.1	8.9 ±0.4	10.2 ±0.5	23.7 ±0.6
5	6.4±0.7	6.7 ±0.2	9.8 ±0.4	15.9 ±0.6	22.0 ±0.4
6	7.2±0.7	10.9 ±0.3	12.6 ±0.5	14.6 ±0.5	19.8 ±0.5
7	9.5±0.8	16.7 ±0.4	17.7 ±0.5	14.6 ±0.6	12.7 ±0.4
8	10.2±0.9	21.3 ±0.4	20.6 ±0.3	13.4 ±0.6	6.8 ±0.2
9	9.6±0.8	16.7 ±0.5	13.8 ±0.7	10.9 ±0.6	1.2 ±0.1
10	10.0±0.5	10.9 ±0.3	7.2 ±0.5	7.1 ±0.5	0.05±0.05
11	10.3±0.9	5.3 ±0.2	2.4 ±0.2	3.8 ±0.3	···
12	9.9±0.9	1.6 ±0.1	0.5 ±0.1	1.3 ±0.2	···
13	6.6±0.7	0.3 ±0.1	0.19±0.06	0.39±0.08	···
14	5.5±0.7	0.08±0.04	···	0.11±0.06	···
15	2.1±0.4	···	···	···	···
16	1.3±0.3	···	···	···	···
17	0.8±0.3	···	···	···	···
Xe*N* (*I*)	Hg*N* (*F*)	Xe*M* (*G*)	Xe*M* (*H*)	Xe*N* (*I*)	Hg*O*, $N_{\text{VI,VII}}$ (*J*)
1	3±1	1.0±0.5	1.5 ±0.2	5 ±1	5±2
2	21±2	8.1±0.6	9.1 ±0.5	40 ±1	49±2
3	20±2	7.4±0.7	9.6 ±0.4	28 ±1	35±2
4	22±1	31.8±0.8	33.9 ±0.6	21 ±1	8±2
5	21±2	26.0±1.2	26.2 ±0.9	4.8±0.5	3±1
6	7±1	16.5±0.9	14.9 ±0.5	1.2±0.4	···
7	5±1	5.6±0.6	3.6 ±0.2	···	···
8	1±1	3.2±0.5	1.1 ±0.1	···	···
9	···	0.4±0.3	0.13±0.05	···	···

[a] The gas irradiated, the principal shell where most of the initial vacancies are created, and the x-ray source (the last named is designated by a capital letter enclosed in parentheses and is described in Table I).

to know the energy of the x ray, and the differential cross sections at that energy. We have discussed the choice of the x-ray energy in the experimental section. The differential cross sestions for the *L* and *M* shells of Xe and Hg have been obtained from formulas originally derived by Stobbe and Hall.[16] For an estimate of the relative cross sections of the higher principal shells, we have generalized Jönsson's rule (see reference in footnote 7) by stating that the relative cross section of the different primary shells are proportional to the binding energies of the *s* electrons in the respective shells. In the study of Hg and the *N* shell of Xe, where not enough data are available for a complete analysis in terms of Eq. (1), we have simplified the equation to read *n* rather than *nl*, assuming that the charge spectrum resulting from a vacancy in each primary shell is independent of the x-ray energy. This is not strictly true, since the photoelectron cross section of the various subshells is dependent on the energy, and there are differences in the charge spectra depending on the subshell in which a vacancy is formed. But such an analysis allows one at least a qualitative picture of the atomic readjustment to a hole in a given primary shell as produced by an x ray whose energy is large enough to eject any electron in that shell.

In Table III we have listed the cross sections calculated by the various methods described above for each of the runs on Hg and Xe.

V. CHARGE SPECTRA FOR THE INDIVIDUAL ATOMIC SHELLS

With the help of the analysis described in the preceding section we have used data on the charge spectra resulting from x-irradiation of rare gases for determining the relative abundances of ions that are the conse-

TABLE III. Relative photoelectric cross sections[a] for various shells of Xe and Hg.

Atom	X-ray source[b]	L_{I}	$L_{\text{II, III}}$	M_{I}	$M_{\text{II, III}}$	$M_{\text{IV, V}}$	*N*	*O*
Hg	*A*	0.18	0.58	0.05	0.12	0.02	0.04	0.01
Xe	*B*	0.22	0.59	0.05	0.10	0.01	0.03	0.00
Xe	*C*	···	0.80	0.04	0.11	0.02	0.03	0.00
Hg	*D*	···	···	0.10	0.37	0.32	0.18	0.03
Xe	*E*	···	···	0.11	0.42	0.31	0.15	0.01
Hg	*F*	···	···	···	···	···	0.87	0.13
Xe	*G*	···	···	···	0.39	0.45	0.15	0.01
Xe	*H*	···	···	···	···	0.72	0.26	0.02
Xe	*I*	···	···	···	···	···	0.94	0.06
Hg	*J*	···	···	···	···	···	···	1.00[c]

[a] As calculated using Stobbe's formulas (cf. Ref. 16) and other procedures discussed in Sec. IV.

[b] See Table I.

[c] With the x-ray source (*J*) vacancies are also produced in the $N_{\text{VI,VII}}$ shell. (See Ref. 18).

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[16] For a complete summary of these formulas see A. J. Bearden, *Calculated Atomic Photoeffect Cross Section by Modified Stobbe Theory* (University of California at San Diego, La Jolla, California, 1965). However, the formulas in the region between the experimental and calculated binding energies, viz., Eqs. (9), (11), (13), (15), and (17) are in error. For these regions we have extrapolated results calculated at higher energies. *Note added in proof*. A revised version of this report appeared in J. Appl. Phys. **37**, 1681 (1966).

TABLE IV. Charge spectra of ions resulting from the readjustment to the sudden vacancy in the K, L, M shells of the rare gases.

Charge	Shell									
	HeK	NeK	NeL	ArK	ArL_{I}	Ar$L_{\mathrm{II,III}}$	ArM	KrM_{I}	Kr$M_{\mathrm{II,III}}$	Kr$M_{\mathrm{IV,V}}$
1	96.5	1.0	87.3	0.7	0	0	85.5	0	0.0	0
2	3.5	73.6	11.9	10.5	2	74	13.5	13	9	60
3	...	22.0	0.8	7.8	72	24	1.0	42	40	39
4	...	3.1	...	42.7	24	2	...	30	45	1
5	...	0.3	...	25.0	2	...	...	13	6	...
6	...	...	...	10.3	...	...	...	2	...	...
7	...	...	...	2.4	...	...	...	...	...	...
8	...	...	...	0.6	...	...	...	...	...	...
	KrK	KrL_{I}	Kr$L_{\mathrm{II,III}}$	XeK	XeL_{I}	Xe$L_{\mathrm{II,III}}$	XeM_{I}	Xe$M_{\mathrm{II,III}}$	Xe$M_{\mathrm{IV,V}}$	
1	1	0.3	<0.5	0.3	<1	<2	<2	0.5	<0.8	
2	1.5	0.1	1	<0.3	<1	<2	<2	4	<3	
3	6	0.3	3	0.3	<1	3	<2	5	2	
4	17	1.0	29	5	<1	5	<4	30	37	
5	19	5	37	4	<1	7	10	26	33	
6	16	34	21	11	2	11	30	19	20	
7	13	40	8	17	10	19	34	9	5	
8	13	17	1	23	21	24	17	6	1.5	
9	10	2	...	16	24	17	4	0.8	0.2	
10	4	0.3	...	11	21	9	0.2	...	...	
11	1	...	...	6	13	3	...	...	...	
12	0.1	...	...	3	5	0.6	...	...	...	
13	...	...	...	2	1	0.2	...	...	...	
14	...	...	...	1.3	0.3	...	...	...	...	
15	...	...	...	0.6	...	...	...	...	...	
16	...	...	...	0.3	...	...	...	...	...	

quence of a vacancy in the K, L_{I}, $L_{\mathrm{II,III}}$, M_{I}, $M_{\mathrm{II,III}}$, and $M_{\mathrm{V,V}}$ shells of the rare gases from He to Xe. The data used for Xe have been taken from Table II of this paper, and for the lighter elements from previous work.[2,4,8–10] Included in the studies of the lighter elements are comparison of the data with theoretical calculations of Auger transitions, which were also of help in determining individual charge spectra. In order to

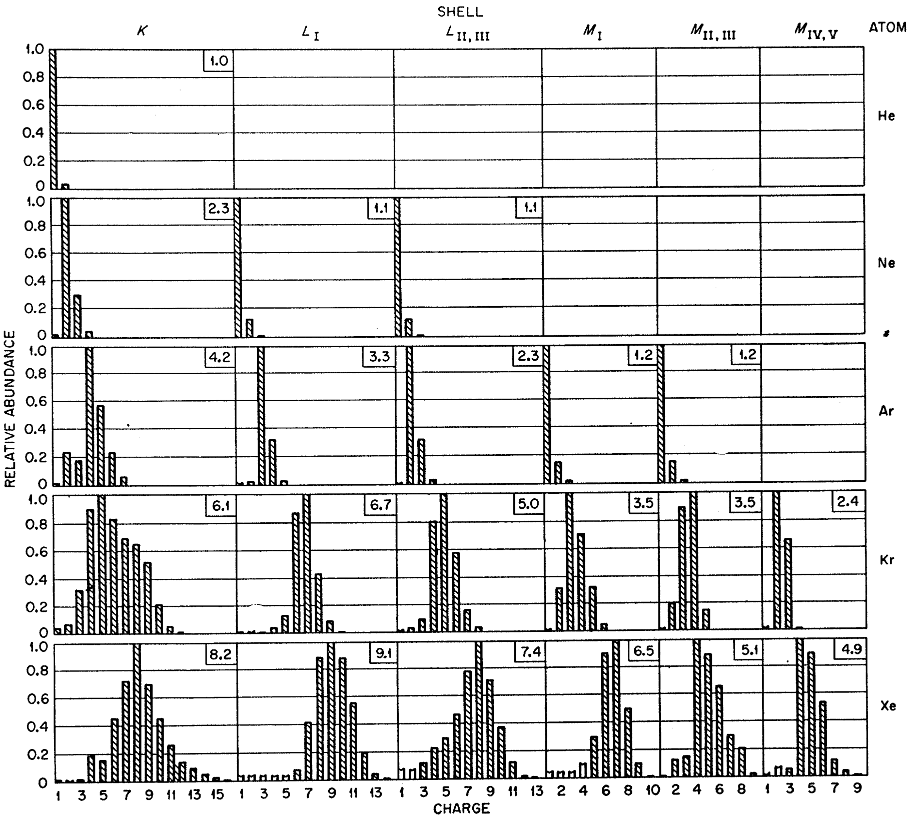

FIG. 1. The relative abundances of ions that are formed as the consequence of a sudden vacancy in the K, L, and M shells of the rare gases. The average charge is given for each spectrum in the upper right-hand corner. The bars containing a notch on top represent an upper limit to the designated intensity.

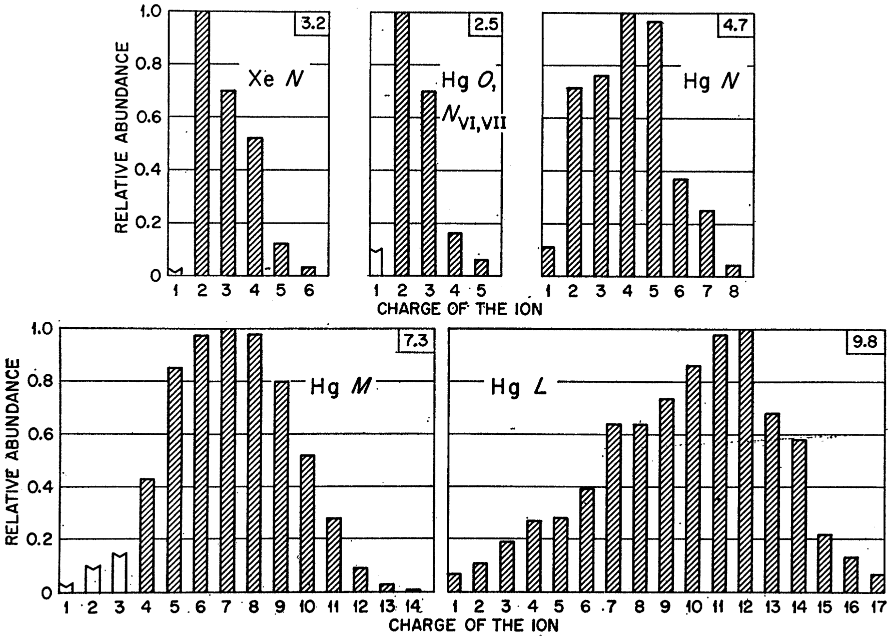

FIG. 2. The relative abundances of ions that are formed from photo-ionization in various principal shells of Xe and Hg. The x rays used to excite the following shells: HgL, HgM, HgN, HgO, and XeM, had the following respective energies in keV: 17.5, 4.5, 1.5, 0.85, 0.22, and 0.24. The average charge is given for each spectrum in the upper right-hand corner. The bars containing a notch on top represent an upper limit to the designated intensity. The HgO shell also contains a considerable contribution from the $N_{\text{VI,VII}}$ shell.

obtain the charge spectrum from a K vacancy in Xe, we included data taken by Pleasonton and Snell[11] on the internal conversion of Xe^{131m}. The results on the rare gases are listed in Table IV in terms of % abundance, and displayed as histograms in Fig. 1, with the peaks normalized to 1.0. In general, the high end of the charge spectra was subject in the analysis to less uncertainty than the lower end. The average charge[17] is also given in Fig. 1 for each spectrum in the upper right-hand corner.

On viewing the spectra in Fig. 1, one may arrive at the following generalizations: (1) We usually observe only one peak for a given charge spectrum, while the intensities of the remaining ions are more or less symmetrically distributed, at least for the more complex spectra. But we also see in the K shell of Ar and Xe slight dips, and in the K shell of Kr a rather large shoulder on the higher charge side, which are evidence for competing vacancy cascades. (2) The heavier the atom and the lower the shell in which an initial vacancy is formed, the higher will be the average charge and the more complex will be the charge spectrum. Exceptions to this rule are seen in the K shells of Kr and Xe, which have lower average charges than those in the L_{I} shells, although the K shells do have larger abundances of the very highly charged ions. These exceptions are caused by radiative transitions, which transfer the original K vacancy to higher shells without ionization.

Let us next turn to the results of producing holes in the principal shells of Hg and the N shell of Xe, which are presented in Fig. 2. These charge spectra were obtained from data[18] given in Table II. Since a charge spectrum of a primary shell is dependent on the distribution of vacancies among the subshells, the results are not general, but rather correspond roughly to what one may expect from x rays whose energies are between the given shell and the next lower primary shell. The relative photoelectric cross sections of the subshells as calculated for specific x-ray energies may be found in Table III for the L_{I}, $L_{\text{II,III}}$, M_{I}, $M_{\text{II,III}}$, and $M_{\text{IV,V}}$ levels. Similar calculations have not been made for the higher shells, but the data themselves may be used to yield information. For example, a doubly charged ion can be identified with a vacancy in the $N_{\text{IV,V}}$ level in the case of Xe, since only one Auger process is energetically allowed in the filling of the vacancy, while a hole found in the other N subshells would, because of the possibility for Coster-Kronig transitions, usually give rise to more than one Auger process. Thus, from the high relative abundance of Xe^{2+} in the spectra for the N shell, it would seem that the cross section for the d subshell is surprisingly large. However, this conclusion is compatible with experimental studies[9,19] on Kr and Xe and with recent calculations by Cooper[20] on the $M_{\text{IV,V}}$ shell of Kr and the $N_{\text{IV,V}}$ shell of Xe using self-consistent-field (SCF) wave functions.

Finally, we note in Fig. 2 that the L shell of Hg appears to be made up of two spectra, one with a peak

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[17] The average charge is defined as $q=\sum_n I_n q_n/\sum_n I_n$, where I_n and q_n are the intensity and charge of the nth ion.

[18] From analogy with studies of the outer shells of other rare gases (cf. Ref. 10), we have also assigned to the outer shell of Xe the distribution: charge-1, 0.8; and charge-2, 0.2. In addition we have assumed that the measured charge spectrum for vacancies in the HgO $N_{\text{VI,VII}}$ (run J) shell is not significantly different from producing vacancies in the O shell alone.

[19] A. P. Lukirskii, I. A. Brytov, and T. M. Zimkina, Opt. i Spectroskopiya **17**, 234 (1964) [English transl.: Soviet Phys.—Opt. Spectry. **17**, 438 (1964)]; D. L. Ederer, Phys. Rev. Letters **13**, 760 (1964).

[20] J. W. Cooper, Phys. Rev. Letters **13**, 762 (1964) for Xe, and J. W. Cooper (private communication) for Kr.

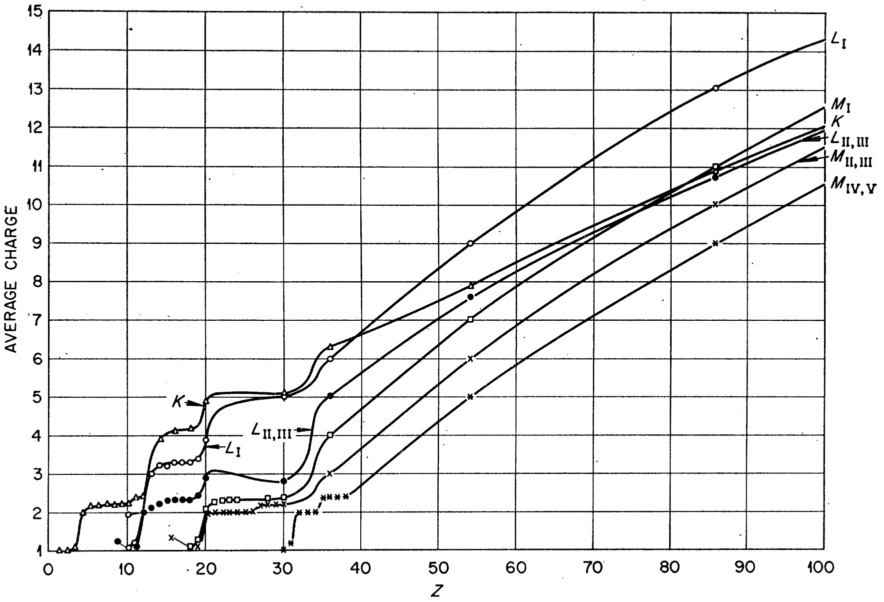

FIG. 3. Estimated average charge as the result of a sudden vacancy in the K, L, and M shells as a function of the atomic number.

at about charge 7, and the other about charge 12. This is reasonable, if we assign the high peak to vacancies in the $L_{\rm I}$ or $L_{\rm II,III}$ shells that are filled by nonradiative transitions, while the lower peak can be said to arise when a vacancy in the $L_{\rm II,III}$ shell is transferred by means of a radiative transition to the $M_{\rm IV,V}$ shell (which occurs about $\frac{1}{3}$ of the time).

VI. ESTIMATE OF THE AVERAGE CHARGE

We now have enough data on various charge spectra of atoms to allow us to make some predictions regarding the extent of ionization following a hole in any shell of any atom. For simple vacancy cascades that occur in the lighter atoms one may compute the charge spectra based on knowledge of (1) the Auger and radiative transition rates and (2) electron shake-off probabilities. This has been done for Ne, Ar, and Kr with a fair degree of success.[2,4,8,9] But such calculations are time-consuming and require knowledge of transition rates that are not always available; and as the atom becomes larger, the calculations become completely unwieldy. However, we should like to suggest here a recipe for estimating the average charge resulting from an inner shell vacancy that will fit our present data and that may be used to provide a reasonable guess for other atoms.

The recipe is as follows: the average charge resulting from a vacancy in a rare gas atom is equal to the number of shells (differentiated by the principal and angular-momenta quantum number) above the shell where the vacancy is formed plus one for the initial vacancy, with the exception that the valence shell is counted as one. Radiative transitions are roughly accounted for by transferring a fraction of the K vacancies to the $L_{\rm II,III}$ shell and a fraction of the $L_{\rm II,III}$ vacancies to the $M_{\rm IV,V}$ shell according to the fluorescence yield.[21] To obtain the average charge for the other atoms, a smooth curve may be drawn through the calculations for the rare gases.

In Fig. 3 we have plotted the results from this recipe for the K, L and M shells. However, for the lighter elements we have not been satisfied with a smooth curve connecting the rare gases, since as one examines the extent of ionization for a given inner-shell vacancy as a function of the atomic number, he may often find, in the case of the lighter elements, abrupt changes in the average charge rather than a gradual increase with increasing Z. On the other hand, when one goes to heavier atoms the vacancy cascades become more complex (at least when the initial hole is in one of the lower shells) and one may expect that the step-wise changes will begin to smooth out into more gradual changes. Fortunately, it has been possible for the lighter elements to make a more sophisticated guess[22] as to the average charge arising from a given atomic vacancy, based on which Auger processes are energetically possible,[23] on the radiative and Auger transition rates as calculated by Rubenstein,[24] and on an estimate of elec-

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[21] A. H. Wapstra, G. J. Nijgh, and R. Van Liesbout, *Nuclear Spectroscopy Tables* (North-Holland Publishing Company, Amsterdam, 1959), pp. 81, 87.

[22] For more details on how these estimates are made, see Refs. 2, 4, 8, 9.

[23] This has been determined with the help of binding energies of the shells considered in the transition. See J. A. Bearden and A. F. Burr, U. S. Atomic Energy Commission Division of Technical Information, Oak Ridge, Tennessee, Report No. NYO-2543-1, 1965 (unpublished); for the ionization potentials see C. E. Moore, *Atomic Energy Levels*, U. S. Government Printing and Publishing Office, Washington, D. C., 1958), Vol. III; SCF wave functions, see F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[24] R. A. Rubenstein, Ph.D. thesis, University of Illinois, 1955 (unpublished).

tron shake-off.[25] The points shown in Fig. 3, not corresponding to the rare gases, are the result of these "more sophisticated estimates."

In Table V we have compared the average charge resulting from inner-shell vacancies as obtained from analysis of the experimental data with calculations based on the recipe and on the curves given in Fig.3. In addition "more sophisticated estimates" are given in parentheses. We have also included recent measurements[13] on the charge spectrum of ^{226}Th following internal conversion. The initial vacancy distribution in Th has been derived, assuming an E2 transition, from internal conversion coefficients.[26] The agreement in Table V between the observations and the calculated values is, in general, fairly good.

TABLE V. Comparison of average charges arising from inner-shell vacancies in atom.

Atom	Z	Shell	Observed[a]	Calculated[b]
He	2	K	1.0	1.0
Ne	10	K	2.3	2.0 (2.2)
Ne	10	L	1.1	1.0 (1.1)
Ar	18	K	4.2	3.8 (4.2)
Ar	18	L_{I}	3.3	3.0 (3.3)
Ar	18	$L_{\mathrm{II,III}}$	2.3	2.0 (2.3)
Ar	18	M	1.2	1.0 (1.1)
Kr	36	K	6.1	6.3 (6.1)
Kr	36	L_{I}	6.7	6.0 (6.8)
Kr	36	$L_{\mathrm{II,III}}$	5.0	5.0 (5.0)
Kr	36	M_{I}	3.5	4.0 (3.3)
Kr	36	$M_{\mathrm{II,III}}$	3.5	3.0 (3.4)
Kr	36	$M_{\mathrm{IV,V}}$	2.4	2.0 (2.4)
Xe	54	K	8.2	7.9
Xe	54	L_{I}	9.1	9.0
Xe	54	$L_{\mathrm{II,III}}$	7.4	7.6
Xe	54	M_{I}	6.5	7.0
Xe	54	$M_{\mathrm{II,III}}$	5.1	6.0
Xe	54	$M_{\mathrm{IV,V}}$	4.9	5.0
Hg	80	L	9.8	10.7
Hg	80	M	7.3	9.0
Th	90	(K,L,M,N)[c]	11.3	10.8

[a] From the analysis discussed in Sec. IV except for Th, which was taken from data on ^{226}Th (cf. Ref. 13).

[b] As obtained from recipe for rare gases described in Sec. VI or interpolated from curves in Fig. 3. Values in parentheses are obtained from "more sophisticated estimates" also described in Sec. VI.

[c] Initial vacancy distribution in percent as calculated from internal conversion coefficients is as follows: K, 2; L_{I}, 2; $L_{\mathrm{II,III}}$, 59; M_{I}, 1; $M_{\mathrm{II,III}}$,28; and $N_{\mathrm{II,III}}$, 8.

VII. THE EXTENT OF MULTIPLE IONIZATION IN A CONDENSED PHASE

All our results have referred to an isolated atom. What may one expect if the atom in which a hole has been formed is surrounded by other neighboring atoms? Some answers to this question may be found in the study of molecular gases in which one of the atoms has undergone an inner-shell ionization. For example, recent results[27] have been obtained on CH_3I, C_2H_5I, HI, and $Pb(CH_3)_4$ in which both the relative abundances and recoil energy of the resultant fragment ions were measured. What we may say from these studies and from our knowledge of Auger transitions is the following: In the atomic readjustment to an inner shell vacancy the first part of the vacancy cascade is relatively unaffected by the surrounding atoms. Although there is a possibility that electrons from other atoms could participate in the vacancy cascade, Auger processes usually occur between neighboring shells. Thus, the vacancy cascade generally proceeds from the initial hole, shell by shell, until a large number of vacancies have reached the outside of the atom, which can then be filled by a transfer of electrons from neighboring atoms. This transfer may be accompanied by still more auto-ionization.

The conclusions reached above for gaseous molecules also apply to the condensed media, in that the initial stages of the vacancy cascade are essentially unaffected by the media. When the vacancies have reached the outer shells, the phenomena of electron transfer and additional auto-ionization are quite complex. Ritchie,[28] for example, has recently discussed the phenomenum of Auger processes within the conduction band. An additional consideration also ought to be made, especially in the case of metals, namely, that effective neutralization may occur as soon as each vacancy occurs in the conduction band, so that the full charge never builds up for the atom undergoing a vacancy cascade.

In general, the charge spectrum obtained for an isolated atom readjusting to an inner-shell vacancy can be taken as a measure of the number of electrons lost in the vacancy cascade that is terminated when vacancies reach the outer shells of the atom, but does not include effects that can follow the formation of holes in the outer shell.

VIII. CONCLUSION

Data are now available on the relative abundances of ions formed as the result of an inner shell vacancy in various shells and subshells for a variety of atoms from $Z=2$ to $Z=80$. From these data we have derived some rules for estimating the average charge arising from a vacancy in any shell of any atom. The problem of how a highly charged ion will affect its surrounding in a condensed media is a more complex one, but, at least, a reasonable estimate of the initial extent of ionization following an inner shell vacancy is now possible.

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[25] Single electron shake-off probabilities and how to estimate them may be found, for example, in Refs. 2 and 4.

[26] M. E. Rose, *Internal Conversion Coefficients* (North-Holland Publishing Company, Amsterdam, 1958).

[27] T. A. Carlson and R. M. White, in *Proceedings of a Symposium on Chemical Effects in Nuclear Transformation, Austria, 1964* (International Atomic Energy Agency, Vienna, 1965), Vol. I, p. 23; also J. Chem. Phys. 44, 4510 (1966). Results on C_2H_5I and $Pb(CH_3)_4$ have not yet been published.

[28] R. H. Ritchie, J. Appl. Phys. (to be published).