Satellite structure in the x-ray photoelectron spectra
of rare gases and alkali-metal halides*

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The photoelectron spectra as the result of photoionization in the various subshells of Ar, Kr, and Xe have been studied using Al$K\alpha$ (1487 eV), Mg$K\alpha$ (1254 eV), and in some cases ZrM_ζ (151 eV) x rays. In addition to the main photoelectron peaks there appears satellite structure at slightly lower kinetic energy. When photoionization occurs in the core levels, this structure can be explained as an electron shakeup in terms of the sudden approximation, and the experimental results are compared with Hartree-Fock calculations of the expected excited states. When photoionization occurs in the valence shell, two-electron excitations leading to the configuration-interaction states $ns^2 np^4 nd^1 \, {}^2S$ are found to be the dominant processes. Photoelectron spectra were also taken of the valence shell of solid alkali-metal halides, and the satellite structure compared with that of the rare gases. From our results similar phenomena seem to occur with the alkali-metal ions, although the intensities are greater than in the case of the rare gases.

I. INTRODUCTION

The kinetic energy of a photoelectron ejected from an atom is given as

$$E_e = h\nu - E_B , \qquad (1)$$

where $h\nu$ is the photon energy and E_B is the ionization potential, which may be defined as

$$E_B = T_f - T_i , \qquad (2)$$

where T_i and T_f are the total energies of the initial and final states corresponding to the neutral atom and resultant ion. On assumption of the validity of single-electron orbitals, E_B can be taken as the binding energy of orbital nlj if the final state is the ground state of an ion with a vacancy in the nlj subshell. For a monochromatic source of photons, photoelectron peaks will occur, corresponding to the various binding energies of the different subshells of the irradiated atom. We shall call these the "normal" photoelectron peaks. There also occur satellite lines associated with each of the normal peaks due to transitions to excited states. In these cases T_f in Eq. (2) became T_f^* and the satellites appear at kinetic energies $T_f^* - T_f$ below the normal line.

In order to understand the nature of the excitation processes leading to photoelectron satellites we have made a comprehensive study of these lines for Ar, Kr, and Xe as a function of the orbital in which photoelectron ejection occurs. Results were obtained at $h\nu = 1487$, 1254, and

151 eV. Earlier studies of this nature have been made on He[1-4] and Ne,[2,5-8] as well as some preliminary work on Ar.[2] It has been the intention of this investigation to concentrate on problems associated with the heavier rare gases. The data will be divided into two parts: (i) photoionization in the inner or core shells and (ii) photoionization in the outer or valence shells. In the first instance we shall examine the satellite lines as a function of core vacancy and show that the results are consistent with the behavior expected from electron shake-up. In the second instance, electron shake-up can also occur; but the probability is strongly influenced by electron correlation. In addition, we shall show that there also may arise excited states, which involve two-electron excitation in conformity with configuration-interaction states.

Finally, data on the photoionization in the outer s and p subshells of alkali-metal ions will be presented and compared with the earlier work of Wertheim and Rosencwaig.[9] The alkali-metal ions are isoelectronic with the rare gases and one might expect analogous behavior. Comparison of the satellite structure found in the photoelectron spectra of the alkali-metal halide salts will be made with that of the rare gases, and qualitative similarities pointed out.

II. EXPERIMENTAL

The photoelectron spectra were obtained with an electron spectrometer employing double-

focusing spherical plates. The instrument is located in the Physics Division of the Oak Ridge National Laboratory. Design and operation of this spectrometer have been given elsewhere.[10] The slits and baffles were adjusted to give a spectrometer resolution of 0.1% full width at half-maximum. The x-ray source is equipped with exchangeable anodes so that the samples could be irradiated in separate experiments with characteristic x rays of Al$K\alpha$ (1486.6 eV), Mg$K\alpha$ (1253.6 eV), and for some specific studies, Zr$M\zeta$ (151.4 eV). Measurements were taken with the angle θ between the direction of the photon beam and direction of the outgoing photoelectron equal to 90°.

Studies were made on both gases (rare gases) and solids (alkali-metal halide). The gases, Ar, Kr, and Xe, were obtained commercially and had purities better than 99.9%. The salts were reagent grade and used without further purification. The hygroscopic CsCl was loaded under argon atmosphere and transferred to the spectrometer in a vacuum-tight double-valve transport chamber.

For studies on the gases there was a continuous flow of gas through the source volume. The flow rate was controlled by a variable leak valve. The pressure in the source volume was maintained at approximately 10^{-2} Torr, while that in the spectrometer was about 10^{-5} Torr. Under these pressure conditions peaks arising from inelastic scattering of electrons are rather small. Their presence was corrected for by examining the intensities and shapes for inelastic scattering in separate experiments using an electron gun with electron energies and gas pressures that closely duplicated the conditions under which photoelectron data were taken.
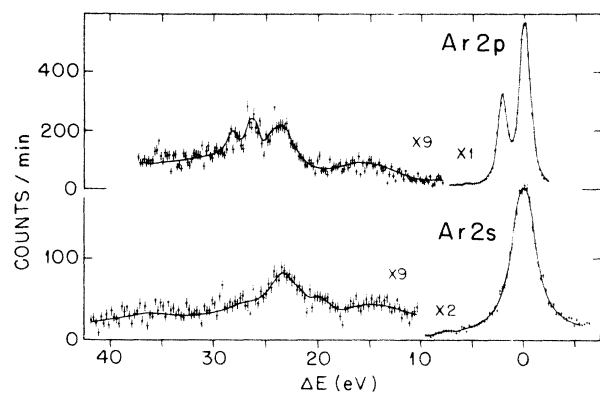
For studies on solids the salts were mounted with double-stick adhesive tape on a multiple-position sample holder. Characteristic energy losses, resulting primarily from plasmon excitation, were estimated observing other lines in the spectrum. It is assumed that the shape and relative intensity of the characteristic energy loss is independent of the source of the photoelectron, except that the relative intensity of the characteristic energy-loss spectrum to the main line varies approximately as $1/\sqrt{E_e}$.[11]

The *absolute* photoelectron energies were obtained only approximately, but special care was taken in determining the *relative* energy splitting between the "normal" photoelectron peak and its satellite. Areas are taken for comparison of intensities. The large error quoted is principally due to uncertainties in the determination of background.

III. RESULTS AND DISCUSSION

A. Inner-shell vacancies

Data were taken on the satellite structure in the photoelectron spectra resulting from photoionization in the core shells of Ar, Kr, and Xe. In Figs. 1–3 the spectra resulting from photoionization in the $2s$ and $2p$ subshells of Ar, the $3p$ and $3d$ subshells of Kr, and the $3d$ and $4d$ subshells of Xe are shown. From the energy separation between the "normal" or principal peak and the satellite lines, one obtains the energy of excitation; and from the relative intensity of the satellite line to the normal peak, one obtains the probability of excitation (assuming similar angular distribution for the photoelectron corresponding to the satellite lines and normal peak).
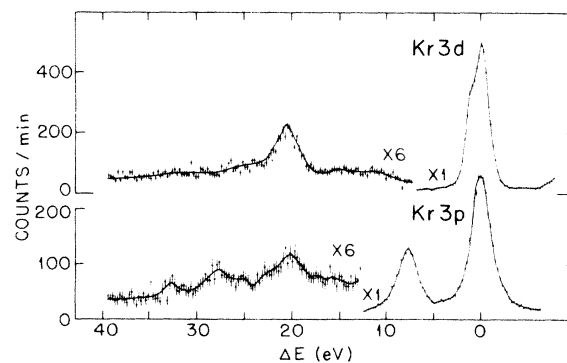

FIG. 1. Photoelectron spectra of argon ionized in the $2s$ and $2p$ subshells, using Mg$K\alpha$ x rays. Energies are given relative to "normal" peak at E_e^0, viz. $E_e^0 - E_e$, where E_e is the kinetic energy and E_e^0 for Ar $2s$ and Ar $2p$ is, respectively, 928 and 1005 eV.

FIG. 2. Photoelectron spectra of krypton ionized in the $3p$ and $3d$ subshells, using Mg$K\alpha$ x rays. Energies are given relative to "normal" peak at E_e^0, viz. $E_e^0 - E_e$, where E_e is the kinetic energy and E_e^0 for Kr $3p$ and Kr $3d$ is, respectively, 1040 and 1160 eV.

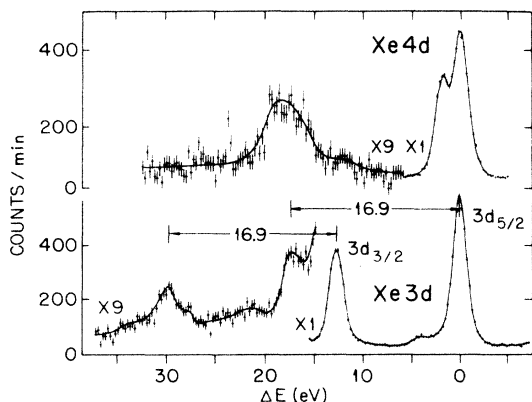FIG. 3. Photoelectron spectra of xenon ionized in the 3d and 4d subshells. Energies are given relative to "normal" peak at E_e^0, viz. $E_e^0 - E_e$, where E_e is the kinetic energy and E_e^0 for Xe 3d using Mg$K\alpha$ x rays is 579 eV and for Xe 4d using Al$K\alpha$ x rays is 1419 eV. The photoelectron peaks due to the $3d_{5/2}$ and $3d_{3/2}$ subshells are clearly separated and their satellite structure occurs 16.9 eV below the respective peaks.

These data are collected in Table I together with earlier results[2,6] on Ne for comparison.

Before the data are discussed, the nature of electron shake-up will be described, since it is believed that this phenomenon is the principal source for the observed satellite structure. The theory of electron shake-up as the result of photoionization has been described in more detail elsewhere.[2,6,12] Briefly, the ejection of a core electron by photoionization causes electrons in the outer shells to see a new central potential. As the result of the change in potential an electron in orbital nlj may be excited to orbital $n'lj$. If the velocity of the ejected photoelectron is substantially greater than the orbital velocity of an outer-shell electron, the sudden approximation may be used to obtain the probability for an electron originally in orbital ψ_{nlj} to find itself in orbital $\psi_{n'lj}$:

$$P_{i \to f} = \left| \int \psi_{n'lj}^*(f)\psi_{nlj}(i)\,d\tau \right|^2 . \tag{3}$$

If one assumes that the atom and resultant ion can be properly described by a product of single-electron wave functions, then $\psi_{n'lj}(f)$ and $\psi_{nlj}(i)$ are single-electron wave functions representing, respectively, the orbital nlj in the initial neutral atom and the orbital $n'lj$ in the ion with a vacancy in the core shell. In the photoionization process the selection rules are those for a dipole transition: $\Delta L = \pm 1$, $\Delta S = 0$. Additional excitations described by Eq. (3) are by means of monopole transitions, $\Delta L = 0$, $\Delta S = 0$, which thus do not affect the selection rules for the over-all pro-

cess: photoionization plus excitation. In electron shake-up, an electron in the valence shell must readjust to a new orbital because of a change in the central potential, but it will not change its angular momentum or spin. As to whether it maintains the same principal quantum number or a higher value depends on the overlap integral given in Eq. (3).

The consequences of the model of electron shake-up described above are the following: (i) The probability of electron shake-up is independent of the photoelectron energy as long as one is in the region covered by the sudden approximation. (ii) Since the removal of a core electron changes the central potential by approximately the same amount regardless of which core orbital is involved, the probability for electron shake-up will be independent of the nature of the core-shell vacancy. Actually, complete shielding is approached asymptotically as one reaches deeper into the core, as likewise is the shake-up probability. (iii) The energy required for promoting electron excitation in the valence shell by means of electron shake-up depends primarily on the nature of the valence shell, and is independent of the nature of the core vacancy, except for secondary effects of coupling the core vacancy with the vacancy formed in the valence shell.

It ought to be further borne in mind that, although we shall be discussing our data only in terms of electron shake-up from the valence shell, other related processes also occur: viz., (i) electron shake-off from the valence shell and (ii) both electron shake-off and shake-up from core shells. In the first instance, electron shake-off or the excitation of an electron into the continuum state is an important process. However, it is much more difficult to observe in well-resolved photoelectron spectra the continuum distribution of electrons due to electron shake-off than it is to see the discrete lines due to electron shake-up, although it has been accomplished.[5] In the second instance, excitation can occur with core electrons as well as valence electrons, but the probability is much smaller,[13] and the energy of excitation much higher.

Let us now review the experimental data with regard to the generalizations made above. First, with regard to the independence of shake-up on the photoelectron energy, comparison of data taken using Mg and Al $K\alpha$ x-rays (cf. Table I) shows no general trend, but the photoelectron energies are not sufficiently separated to offer any definitive conclusion. Results obtained[14] with CuL x rays also do not suggest a large energy dependence, although the uncertainties

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TABLE I. Excitation energy and intensities of satellite structure in the photoionization of core shells of the rare gases.

Inner-shell vacancy	E_B [a]	E_e^0 [b]	Intensity		Excitation energy (eV)	
			Expt. [c]	Theory [d]	Expt. [e]	Theory [f]
Ne 1s	870.2	617	8.7 ± 0.7	19.6	38.8 ± 0.3 [g]	37.6
1s		384	9.6 ± 0.7	19.6	39.0 ± 0.3 [g]	37.6
Ar 2s	326.3	1161	$\cdots$	14.6	23.4 ± 0.3	22.2
2s		928	8 ± 1	14.6	23.7 ± 0.3	22.2
2s		604	8 ± 2 [h]	14.6	$\cdots$	$\cdots$
Ar 2p	248.5	1238	7 ± 1	15.4	25.3 ± 0.3	20.9
		1005	7 ± 1	15.4	24.9 ± 0.3	20.9
		681	7 ± 2 [h]	15.4	$\cdots$	$\cdots$
Kr 3p	214.4	1273	6 ± 1	11.6	20.5 ± 0.3	$\cdots$
		1040	5 ± 1	11.6	20.2 ± 0.3	$\cdots$
Kr 3d	93.7	1393	8 ± 1	11.5	20.4 ± 0.3	18.8
		1160	8 ± 1	11.5	20.5 ± 0.3	18.8
Xe $3d_{3/2}$	689.0	798	11 ± 1	12.4	16.9 ± 0.3	15.9
		565	8 ± 1	12.4	16.9 ± 0.3	15.9
Xe $3d_{5/2}$	676.4	811	11 ± 1	12.4	16.9 ± 0.3	15.9
		579	8 ± 1	12.4	16.9 ± 0.3	15.9
Xe 4d	67.5	1419	6.3 ± 0.5	9.6	17.0 ± 0.3	$\cdots$
		1186	5.1 ± 0.5	9.6	16.9 ± 0.3	$\cdots$
		84	6 ± 1	9.6	16.8 ± 0.3	$\cdots$

[a] Binding energies taken from Siegbahn et al., Ref. 6. In the case of Ar 2p, Kr 3p, Kr 3d, and Xe 4d the binding energy for the $l + \frac{1}{2}$ subshell is given.

[b] Photoelectron energies of the "normal" peaks. The following x-ray energies were used: 1487, 1254, 930, and 151 eV.

[c] Total intensity of satellite structure (excluding high-energy satellites due to shake-up in the s shells) relative to "normal" photoelectron peak which is equal to 100.

[d] Calculation of total electron shake-up plus shake-off for the outermost p shell (cf. Carlson and Nestor, Ref. 13) relative to "normal" photoelectron peak which is equal to 100.

[e] As measured from peak of "normal" photoelectron peak to peak of satellite structure.

[f] Calculation of difference of total energies between the free atom and the excited state of ion using nonrelativistic Hartree-Fock program of C. F. Fischer. Calculations made by C. W. Nestor, Jr. The ions have the indicated vacancy in the core shell, and the outer-shell np electrons were excited to the $(n + 1) p$ shell. The unfilled shells were treated in terms of an average configuration.

[g] Average of energy peaks corresponding to $2p^5 3p^1$ (up), $2p^5 3p^1$ (down) (cf. Refs. 2 and 6).

[h] Data taken with $Cu L\alpha$ x rays as obtained by Keski-Rahkonen and Krause, Ref. 14.

caused in subtracting background make this conclusion only tentative. Studies have been made earlier[15] on electron shake-off from the L shell as the result of photoionization in the 1s shell of neon as a function of photoelectron energy. (In electron shake-off the excited electron goes into the continuum rather than into a bound state.) The probability for shake-off remained constant from photoelectron energies of 17.5 down to about 200 eV. Below this energy the shake-off probability rapidly decreased. At a photon energy 65 eV above the K -shell binding energy of neon, shake-off processes were found to be only 20% of their maximum value, but shake-up probabilities[16]

were nearly unchanged from those taken at higher photon energies.

The assertion that the intensity for shake-up will be nearly independent of the nature of the core shell is also borne out in Table I. Specific calculations[17] of electron shake-up have been carried out only for shake-up into the $1s^1 2s^2 2p^5 3p\ ^2S$ (spin-up and spin-down) states of neon. The agreement with experiment is quite good. Unfortunately, such calculations are difficult because wave functions for the excited state of the ion need to be carefully orthogonalized for use in Eq. (3). On the other hand, calculations for the total probability for shake-off plus shake-up

processes are relatively easy to carry out with some precision, since only the ground-state wave function for the ion is required. Such calculations have been done as a function of photoionization in each of the subshells of all the rare gases.[13] The calculated probabilities for shake-off plus shake-up in the outermost p subshell are also listed in Table I. The calculated intensities will always be larger, since they include transitions to the continuum (electron shake-off). It appears that electron shake-up processes account for at least one-half of the excitation expected for the valence-shell electrons. It is interesting to note that the calculations suggest a slight increase in electron shake-up plus shake-off as one goes deeper in the core of Xe, from $n = 4$ to 3, which is reflected in the experimental data. This increase most likely arises from the fact that a core electron does not offer full shielding equivalent to one electron charge until the shell is at least more than one principal quantum number lower than the valence shell.

The energy of excitation due to electron shake-up has been calculated from differences in total energies between the ground state and appropriate excited configuration for the singly charged ion which was taken to be the states representing the first monopole transition of the outermost p orbital. The Hartree-Fock wave-function program of Fischer was used in these calculations.[18] Most calculations were carried out by treating the incompletely filled shells in terms of an average configuration. Some coupling can be expected between the core vacancy and the un-
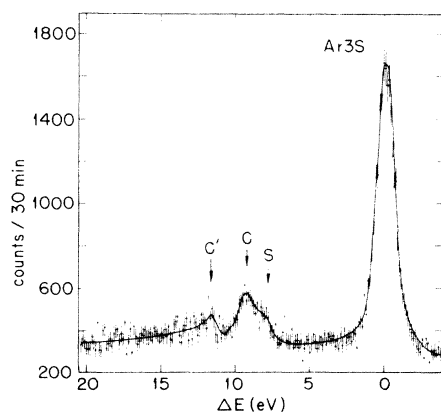

FIG. 5. Photoelectron spectrum of krypton ionized in the valence shell. Energies are given relative to "normal" $4s$ peak at E_e^0, viz. $E_e^0 - E_e$, where E_e is the kinetic energy and E_e^0 for Kr$4s$ using Mg$K\alpha$ x rays is 1240 eV. S and C indicate position of peaks due to electron shake-up and configuration interaction, respectively, as deduced from optical data. The letter A indicates contribution from LMM Auger transitions (cf. Table II for more details).

filled valence shell. The extent of coupling was calculated in the case of neon $1s^1 2s^2 2p^5 3p^1$ and argon $2s^1 2p^6 3s^2 3p^5 4p^1$. In these cases a doublet arises, separated by 3.9 eV, in the case of neon, and 0.7 eV in the case of argon. Though the energies involved in the coupling are not negligible,

FIG. 4. Photoelectron spectrum of argon ionized in the valence shell. Energies are given relative to "normal" $3s$ peak at E_e^0, viz. $E_e^0 - E_e$, where E_e is the kinetic energy and E_e^0 for Ar$3s$ using Mg$K\alpha$ x rays is 1225 eV. S and C indicate position of peaks due to electron shake-up and configuration interaction, respectively (primes indicate higher excited states), as deduced from optical data (cf. Table II for more details).
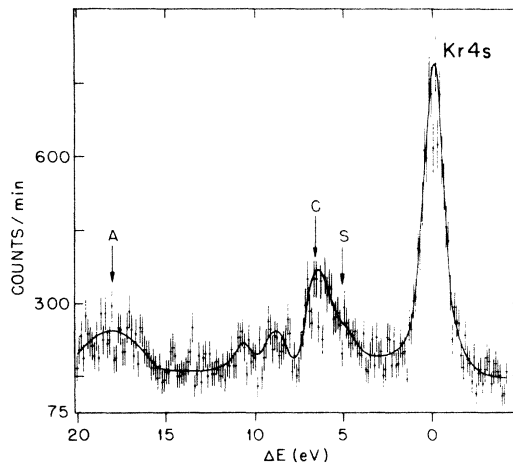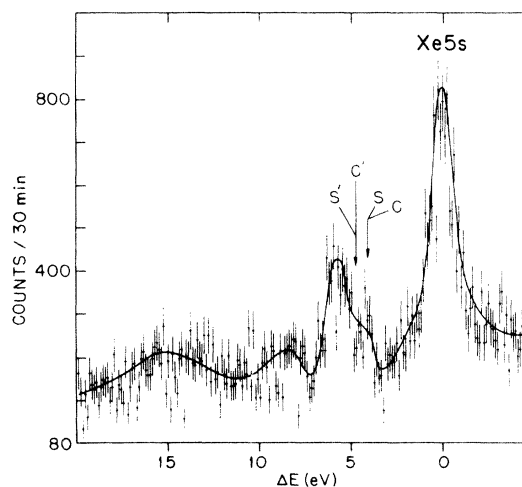

FIG. 6. Photoelectron spectra of xenon ionized in the valence shell. Energies are given relative to "normal" $5s$ peak at E_e^0, viz. $E_e^0 - E_e$, where E_e is the kinetic energy and E_e^0 for Xe$5s$ using Mg$K\alpha$ x rays is 1231 eV. S and C indicate position of peaks due to electron shake-up and configuration interaction, respectively (primes indicate higher excited states), as deduced from optical data (cf. Table II for more details).

TABLE II. Analysis of satellite structure for valence shells of the rare gases.

| Line | Excitation energy | | Configuration | Designation | Intensity[a] | | |
	XPS[b]	Optical[c]			Al $K\alpha$	Mg $K\alpha$	Zr $M\zeta$
Ar3p	0	0	$3s^2 3p^5$	$^2P^0$	145 ± 8	182 ± 10	533 ± 25
Ar3s	13.5 ± 0.1	13.49	$3s^1 3p^6$	^2S	100	100	100
S	21.6 ± 0.2	21.39	$3s^2 3p^4 4p^1$	$4p'\,^2P^0$	3 ± 2	4 ± 2	15 ± 3
C	22.9 ± 0.1	22.82	$3s^2 4p^4 3d^1$	$3d'\,^2S$	19 ± 2	15 ± 2	15 ± 2
C'	25.4 ± 0.2	25.44	$3s^2 3p^4 4d^1$	$4d'\,^2S$	6 ± 3	7 ± 3	8 ± 3
Kr4p	0	0	$4s^2 4p^5$	$^2P^0$	...	466 ± 25	
Kr4s	13.5 ± 0.1	13.51	$4s^1 4p^6$	^2S	100	100	
S	18.4 ± 0.2	18.61	$4s^2 4p^4 5p^2$	$5p'\,^2P^0$	7 ± 2	9 ± 2	
C	20.0 ± 0.1	19.94	$4s^2 4p^4 4d^1$	$4d'\,^2S$	31 ± 3	25 ± 3	
C'	...	20.39	$4s^2 4p^4 6s^1$	$6s''\,^2S$	...	...	
Xe5p	0	0	$5s^2 5p^5$	$^2P^0$	355 ± 20	449 ± 20	
Xe5s	11.3 ± 0.1	11.27	$5s^1 5p^6$	^2S	100	100	
S	...	15.37	$5p^2 5p^4 6p^1$	$6p\,^2P^0$	...	...	
C	15.5 ± 0.2	15.38	$5s^2 5p^4 6s^1$	$6s''\,^2S$	11 ± 3	10 ± 3	
C'	...	16.02	$5s^2 5p^4 5d^1$	$5d'\,^2S$	...	...	
S'	...	16.27	$5s^2 5p^4 6p^1$	$6p'\,^2P^0$	...	...	
	16.9 ± 0.1				62 ± 7	45 ± 5	

[a] Intensities of peaks obtained in XPS data using Al $K\alpha$, Mg $K\alpha$, and Zr $M\zeta$ x rays of, respectively, 1487, 1254, and 151 eV. Intensities given relative to "normal" photoelectron peak corresponding to photoionization in the outermost s shell.

[b] X-ray photoelectron spectra (XPS) data taken from Figs. 4 and 5 and averaged with data of similar runs. Energy is given relative to "normal" photoelectron peak corresponding to photoionization in the outermost p shell.

[c] Energy difference as obtained from optical data [C. E. Moore, Atomic Energy Levels, NBS No. 467 (U. S. GPO, Washington, D. C., 1949, 1952, 1958), Vols. I–III]. Energies are given for the corresponding configuration. In the case of Kr $4s^2 4p^4 4d^1(4d'\,^2S)$ optical data is obtained by L. Minnhager, H. Strihed, and B. Petersson, [Arkiv. Fysik. 39, 471 (1969)].

they are small compared to the total excitation energy. Comparison in Table I between the theoretically calculated excitation energies for the most probable shake-up transition and the peak of the satellite structure shows good agreement. The experimental values closely follow the trends suggested by theory. The theoretical value, however, is always slightly lower than experiment, and this discrepancy is apparent even when the coupled states as in neon can be separated experimentally[2] and compared with calculations for the individual spin-up and spin-down states. One assumes that these differences arise from failure to include electron correlation in the calculations.
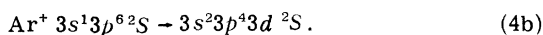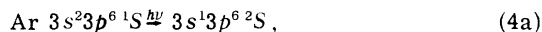
B. Outer-shell vacancies

Excitation as the result of photoionization in the valence shell poses two special problems. First, though electron shake-up can occur, the probability as calculated using single-electron wave functions is often in strong disagreement with experiment,[1] the experimental values being an order of magnitude larger than the calculations. The problem arises from the fact that electron

correlation should be included when photoionization and excitation both occur in the same shell. In the case of helium it has been possible to make calculations[19-22] using Hylleras-type wave functions which explicitly include electron correlation for the bound state. These calculations showed good agreement with experimental results for both electron shake-off and shake-up. Åberg[23] has been able to use the sudden approximation to obtain the high-energy limit using correlated wave functions. Unfortunately, the use of correlated wave functions for calculating electron shake-up has not as yet been extended to the other rare gases.

A second problem is the presence of another source of excitation; a two-electron excitation involving configuration interaction. To give a better account of correlation for a Hartree-Fock solution of an atom, excited configurations are mixed with the ground state. The excited state permissible for mixing should have the same total angular momentum and the same total spin. When evaluating the possible final states of an ion following photoionization, one may consider all data which are permitted for configuration

interaction. Viewing the problem in this fashion, one may consider excited states formed by electron shake-up as a special case of configuration interaction. Another possible configuration-interaction state is illustrated below in the case of photoionization in the $3s$ subshell of argon

$$\text{Ar } 3s^2 3p^6 {}^1S \xrightarrow{h\nu} 3s^1 3p^6 {}^2S, \tag{4a}$$

$$\text{Ar}^+ 3s^1 3p^6 {}^2S \rightarrow 3s^2 3p^4 3d {}^2S. \tag{4b}$$

We can regard the transition to state (4b) as involving double excitation of electrons in the $3p$ orbital to the $3s$ and $3d$ subshells. The importance of this particular configuration-interaction state is that all three orbitals involved in the excitation, $3s$, $3p$, and $3d$, have the same principal quantum number, thus enhancing the probability for a transition to this state because of the large overlap of the participating orbitals.

We are now ready to evaluate the data in conjunction with the discussion given above. The photoelectron spectra of the valence shells of Ar, Kr, and Xe are given in Figs. 4–6. In Table II are given the energies of the principal satellite peaks, together with their suggested designation. Energies for the most probable excited configuration expected from electron shake-up are available from optical data and these have also been listed in Table II. It is obvious that in both argon and krypton the main satellite peaks are in excellent agreement with the excitation energy expected for configuration interaction involving two-electron excitation. Electron shake-up peaks are also detected but are of secondary importance. The satellite structure found in the photoelectron spectra of argon using 151-eV photons shows a marked difference from that found with the Al and Mg$K\alpha$ x rays. The peak ascribed to configuration interaction is small relative to that associated with electron shake-up. This can be understood when it is realized that the main shake-up peak is associated with photoionization in the outer p subshell, while the satellite peak due to configuration interaction arises from s-shell photoionization. In addition to the main contributions to the satellite structure, an additional peak is seen in argon and given a tentative identification as arising from configuration interaction involving a higher principal quantum number. The identification of the xenon satellite structure with optical data based on the most likely excitation processes has not been as definitive as with the argon and krypton, although one expects that configuration interaction would play a major role.

It is interesting to compare our results on the heavier rare gases with studies on neon,[2] includ-
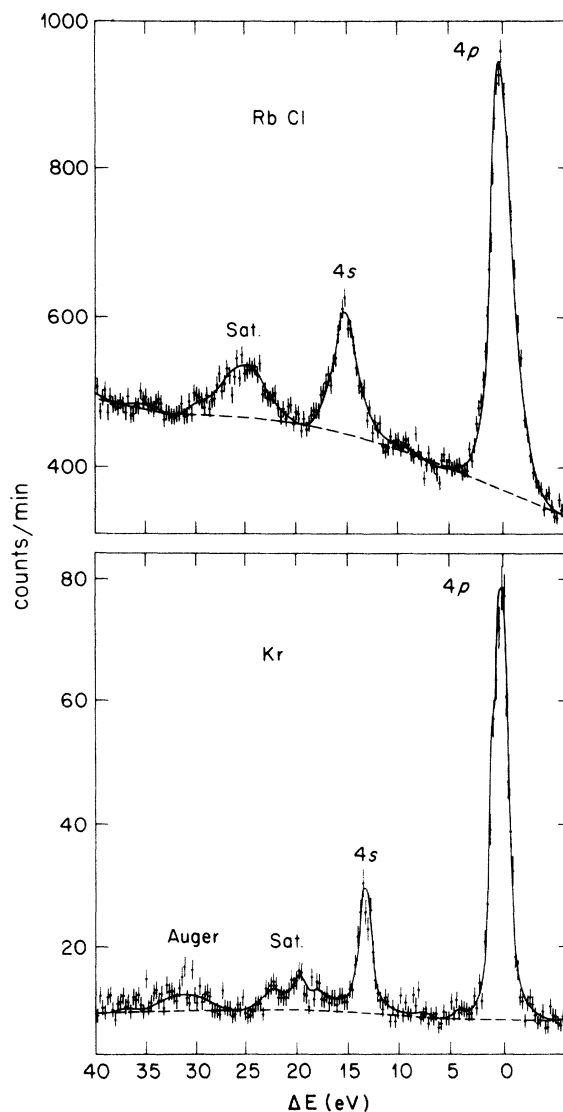

FIG. 7. Comparison of photoelectron spectra from photoionization in the valence shell of Kr and RbCl. Photoelectron energies are given relative to the $4p$ subshell at E_e^0, viz. $E_e^0 - E_e$, where E_e is the kinetic energy and E_e^0 for Kr $4p$ is 1240 eV using Mg$K\alpha$ x rays. Satellite structure is marked Sat. The portion of the Kr spectrum marked Auger comes from some weak LMM Auger processes. The dotted line gives approximate background.

ing a recent investigation[7] of the satellites as a function of photon energy. The conclusion reached in the latter studies was that when photoionization takes place in the L shell of neon, the main satellite contributions come from electron shake-up rather than configuration interaction involving a two-electron excitation. This can be understood from the fact that for neon only the p and s subshells are possible for principal quantum number

TABLE III. Analysis of satellite structure in the photoelectron spectrum of the outermost s and p shells of the alkali-metal ion.

Compound	Line	Excitation energy XPS[b]	Excitation energy Optical[c]	Configuration	Designation	Intensity[a] Al $K\alpha$	Intensity[a] Mg $K\alpha$
NaCl	Na^+ $2p$	0	0	$2s^2 2p^5$	$^2P^0$		41 ± 4
	Na^+ $2s$	32.9 ± 0.3	32.8	$2s^1 2p^6$	^2S		100
	no observable satellite structure						<5
KBr	K^+ $3p$	0	0	$3s^2 3p^5$	$^2P^0$		231 ± 25
	K^+ $3s$	16.1 ± 0.3	16.19	$3s^1 3p^6$	^2S		100
	C	29.8 ± 0.3	29.96	$3s^2 3p^4 4s^1$	$4s''$ ^2S		55 ± 15
	C'	$\cdots$	31.1	$3s^2 3p^4 3d^1$	$3d'$ ^2S		
KCl	K^+ $3p$	0	0	$3s^2 3p^5$	$^2P^0$		229 ± 25
	K^+ $3s$	16.1 ± 0.3	16.19	$3s^1 3p^6$	^2S		100
	C	29.7 ± 0.3	29.96	$3s^2 3p^4 4s^1$	$4s''^2S$		40 ± 8
	C'	$\cdots$	31.1	$3s^2 3p^4 3d^1$	$3d'$ ^2S		
RbCl	Rb^+ $4p$	0	0	$4s^2 4p^5$	$^2P^0$	400 ± 40	410 ± 40
	Rb^+ $4s$	15.9 ± 0.3	16.12	$4s^1 4p^6$	^2S	100	100
	C	$\cdots$	25.30	$4s^2 4p^4 5s^1$	$5s''^2S$		
	C'	26.0 ± 0.3	26.61	$4s^2 4p^4 4d^1$	$4d'$ ^2S	63 ± 10	64 ± 10
	C''	$\cdots$	32.8 [d]	$4s^2 4p^4 5d^1$	^2S		
CsCl	Cs^+ $5p$	0	0	$5s^2 2p^5$	$^2P^0$		275 ± 25
	Cs^+ $5s$	12.9	15.84	$5s^1 5p^6$	^2S		100
	C	22.2	$\cdots$				120 ± 20

[a] Intensity of peaks obtained in XPS data using Al $K\alpha$ and Mg $K\alpha$ x rays. Intensities given relative to "normal" photoelectron peak, corresponding to photoionization in the outermost s shell.

[b] Data taken from x-ray photoelectron spectra of the corresponding salts. Energy is given relative to "normal" photoelectron peak corresponding to photoionization in outermost p shell of alkali metal.

[c] Energy difference as obtained from optical data for singly charged alkali metal ion. [C. E. Moore, Atomic Energy Levels, NBS No. 467 (U. S. GPO, Washington, D. C., 1949, 1952, 1958), Vols. I–III]. Energies are given for the corresponding configuration. No data were found corresponding to configurations for electron shake-up.

[d] Quantum defect calculation of energy by Reader (Ref. 24).

$n = 2$, and thus for the type of two-electron excitation we have been discussing one of the orbitals involved must be in a shell with a higher principal quantum number. This reduces the overlap and consequently the transition probability.

C. Alkali-metal halides

The alkali-metal ions Na^+, K^+, Rb^+, and Cs^- are isoelectronic with the rare gases Ne, Ar, Kr, and Xe. It is, therefore, of interest to compare the satellite lines found in the photoelectron spectra of alkali-metal salts with those of the rare gases. For an example, the photoelectron spectra of Rb^+ and Kr are compared in Fig. 7. In each case satellite structure is found, although the intensity of such structure is much larger in the case of the alkali-metal salts. Wertheim and Rosencwaig[9] were the first to point out the appearance of this satellite structure and to attribute this structure to two-electron excitation in-

volving configuration-interaction states. These conclusions are supported by analogy with our rare-gas data. In Table III we have listed the relative intensities and energies of the normal and satellite lines associated with photoelectron spectra of the outermost s and p shells of other alkali-metal ions. They are in reasonable agreement with the earlier data of Wertheim and Rosencwaig using Al$K\alpha$ x rays. Also listed are the energies for the states corresponding to the free ion as obtained from optical data. Comparison with the data taken on the solids should be taken with some caution, since we are not dealing strictly with free ions. However, the optical data does support the supposition that configur   n interaction plays a major role as wi   _ rare gases. Wertheim and Rosencwaig also suggested that transition in K^+ and Rb^+ to $ns^2 np^4 (n+1)s^1$ ^2S may be important, but Reader[24] has argued that this is unlikely, and that the $ns^2 np^4 nd^1$ configurations as with the rare gases are the most

important excited states. Note that essentially no satellite structure was found with Na$^+$. This is probably, as with neon, due to the fact that one cannot form a configuration interaction state with three subshells all having the same principal quantum number. A comment is required on the larger intensities of satellite peaks found with the alkali-metal halide salts versus the rare gases. There is no reason to expect transitions to excited states of the free ions of the alkali-metal ions to be greater than for the parallel case of the rare gases. For example, we found calculations on electron shake-off in the rare gases gave slightly higher values than the corresponding alkali-metal ions. We believe that the difference between the salts and the rare gases to be a solid-state effect. Perhaps the d electrons in the conduction band of an alkali-metal halide may have a greater overlap with the s and p core subshells than the corresponding overlap of the s, p, and d orbitals in a free gas atom.

IV. CONCLUSION

The nature of electronic excitation accompanying photoionization has been studied by observing the satellite lines found in the photoelectron spectra of the rare gases. When photoionization occurs in the core or inner shells the excitation arises primarily from electron shake-up, which can be understood in terms of the sudden approximation and calculated with the help of single-electron wave functions. The problem is complicated by electron correlation when photoionization occurs in the valence shell. In addition, for the heavier rare gases (argon, krypton, and xenon), double excitation conforming to a configuration interaction state plays the major role. Similar satellite structure occurs with photoelectron spectra of the alkali-metal ion, analogous to the isoelectron rare gas, although the intensities appear substantially larger.

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