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THE RELATION BETWEEN SATELLITE PEAKS IN X-RAY
EMISSION AND X-RAY PHOTOEMISSION SPECTRA*

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ABSTRACT

A unified model is given to explain the satellite structures observed in x-ray emission spectroscopy (XES) and x-ray photoelectron spectroscopy (XPS). This model accounts for electron correlation by the use of configuration interaction, rather than the heuristic "shake-up" approach, and actual eigenstates of the system are considered. The XPS final states, plus its correlation states, serve as the initial states in XES. The final XES states consist of the main state plus its satellites. Two situations are discussed, differing in whether the final XES states have holes in core or valence shells. For core-to-core XES transitions, the correlation-state structure is almost identical in initial and final states. Large satellite intensities may be observed in XPS, but not in XES, in accord with experiment. In core-to-valence XES transitions, the satellite structure should be similar to that observed in XPS, also in accord with experiment. Detailed CI calculations for the 3s spectra of Ar are compared with experiment.

I. Introduction

In the past few years there has been a resurgence of interest in the x-ray emission spectroscopy (XES) of gases and solids.¹⁻³ This has been accompanied by theoretical investigations of the energies and relative intensities of the "diagram lines" in the x-ray spectrum,³⁻⁵ i.e., the peaks which correspond to transitions between two of the primary ionic states of the system. Because both of these states are also observed in x-ray photoelectron spectroscopy (XPS), there have been several discussions about the complementary nature of the information provided by XPS and XES. For example, Manne^{6a} has shown that because XES obeys "effectively" different selection rules, it can be helpful in assigning the photoelectron spectrum.^{6b}

In 1970, Cooper and La Villa⁷ reported a rather broad feature on the low (photon) energy side of the $L_{2,3}(2p_{1/2,3/2} \rightarrow 3s)$ diagram "line" in Ar, K^+ , and Cl^- . Subsequent work by Werme, et al.,⁸ showed that it consisted of several discrete lines and confirmed the earlier assignment of this structure to final states based on the configurations $3s^2 3p^4 nd(^2S)$, $n = 3, 4$. In terms of the models in use in XPS, Cooper and LaVilla noted that the transition could be described as a one-electron transition ($3s \rightarrow 2p$) accompanied by the simultaneous two-electron process $3p^2 \rightarrow 3s3d$. They termed this a "semi-Auger" transition, the XES analog of "shake-up" in XPS. The corresponding "shake-off" process is known as "radiative Auger", and is obtained when nd is replaced with a continuum function ϵd . Radiative Auger processes have recently been reviewed by Åberg.⁹

In this paper we are concerned with the relationship between the discrete satellite structures observed in XPS and XES. Other recent work of interest in this respect is that of Asada, Satoko, and Sugano,¹⁰ and Wood and Urch.¹¹ These workers were primarily concerned with the structure in open-shell systems arising from the distribution of the one-electron transition moment over several ionic multiplets. In contrast, we will be interested primarily in the structure which is not attributable to such "multiplet splitting" origins. Section II reviews some general considerations about the nature of satellite states and the transition moments responsible for photon emission and photoionization. We will find it meaningful to classify the x-ray emission process into core-to-core and core-to-valence-like transitions, the two classes having distinctly different characteristics with respect to the semi-Auger and other satellite transitions. Section III presents the results of SCF and CI calculations of the intensities of "shake-up" and semi-Auger transitions in the 3s subshell of argon. Finally, in Section IV, we discuss these processes in inert gases, alkali halides, and transition-metal complexes.

II. Satellites in XPS and XES

Figure 1 shows a hypothetical state diagram for an ionic species. The states labeled P_1 and P_2 are two of the primary ionic states of the system; associated with each of them is a satellite state, S_1 or S_2 . In a photoemission experiment all four of these states can be reached, and the intensity of, e.g., S_1 relative to P_1 will be governed by the projection of their respective wavefunctions onto the hypothetical

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"frozen-orbital" primary ionic state P_1^{FO} , defined by removing the photoelectron from the initial (neutral) ground state without allowing the passive orbitals to relax (i.e., as in Koopmans' model). For example, if the exact ionic-state wavefunctions are expanded in configurations utilizing the ground state orbitals of the neutral species

$$|P_1\rangle = c_{01}|P_1^{FO}\rangle + \dots \quad (1a)$$

$$|S_1\rangle = c_{11}|P_1^{FO}\rangle + \dots \quad (1b)$$

then the relative intensity of the satellite in the XPS case is given in the high-photon-energy limit by¹²

$$\frac{I(S_1)}{I(P_1)} = \frac{|c_{11}|^2}{|c_{01}|^2} \quad (2)$$

Turning now to the XES process, we note that decay of the ionic states P_1 and S_1 via x-ray emission leads to four distinct possibilities. The transition labeled A in Fig. 1 produces the diagram line, while B corresponds to a semi-Auger peak. Processes C and D are similar, but originate from decay of the satellite state S_1 .

The initial states in this example must have the same symmetry (as do the final states P_2 and S_2), but the allowed transitions between the two groups are, of course, dictated by the dipole selection rules. For the purpose of discussing the relative intensities of these transitions, it will be useful to distinguish the case in which P_1 and P_2 are both core hole-states from that where P_1 is a core hole-state and P_2 is a valence hole-state.

A. Core-Core XES

Let us consider the simplest possible situation, that in which there are two strongly-interacting configurations in each primary ionic state. The wavefunctions for the primary hole state can thus be written as

$$|P_1\rangle = c_{01}|P_1^{FO}\rangle + c_{11}|P_1^{FO}, k \rightarrow \ell\rangle \quad (3)$$

where the last configuration has additional excitation(s) ($k \rightarrow \ell$) relative to the frozen orbital state. In this example, orthogonality requires that the satellite state be described by the wavefunction

$$|S_1\rangle = -c_{11}|P_1^{FO}\rangle + c_{01}|P_1^{FO}, k \rightarrow \ell\rangle \quad (4)$$

with $c_{01} > c_{11}$ and $c_{01}^2 + c_{11}^2 = 1$. The final states can be written similarly:

$$|P_2\rangle = c_{02}|P_2^{FO}\rangle + c_{12}|P_2^{FO}, m \rightarrow n\rangle \quad (5a)$$

$$|S_2\rangle = -c_{12}|P_2^{FO}\rangle + c_{02}|P_2^{FO}, m \rightarrow n\rangle \quad (5b)$$

In the general case, the coefficient c_{01} will not be equal to c_{02} , and the excitation $m \rightarrow n$ will be different from $k \rightarrow \ell$. However, in the case that P_1 and P_2 are both core-hole states, the rearrangements in the valence shell which characterize the satellites should be largely independent of the nature of the hole. The dominant influence is simply the additional ion-core charge experienced in the valence region due to the inner-shell ionization.¹³ Thus the excitations $m \rightarrow n$ and $k \rightarrow \ell$ should be the same, and the configurations ($P_2^{FO}, m \rightarrow n$) and

$(P_1^{FO}, k \rightarrow l)$ should differ by the primary orbital which is missing from the neutral ground state in $|P_2^{FO}\rangle$ and $|P_1^{FO}\rangle$. Furthermore, the amplitudes and phases of the mixing coefficients should be very nearly the same, i.e., $c_{01} \cong c_{02}$, $c_{11} \cong c_{12}$.

In the terms of these approximations, the transition moments for the various processes are (abbreviating c_{01} and c_{02} as c_0 , etc.):

$$\begin{aligned} \text{A: } c_0^2 T + c_1^2 T' &\cong T \\ \text{B: } -c_0 c_1 T + c_0 c_1 T' &\cong 0 \\ \text{C: } -c_0 c_1 T + c_0 c_1 T' &\cong 0 \\ \text{D: } c_1^2 T + c_0^2 T' &\cong T \end{aligned} \quad (6)$$

In these expressions T and T' are the dipole transition moments connecting the configurations,

$$T \propto |\langle P_2^{FO} | \vec{r} | P_1^{FO} \rangle|^2 \quad (7a)$$

$$T' \propto |\langle P_2^{FO}, k \rightarrow l | \vec{r} | P_1^{FO}, k \rightarrow l \rangle|^2, \quad (7b)$$

and we have made the additional assumption that $T \cong T'$. This is very reasonable because both cases involve the same one-electron transition, with only the valence distribution being different.

An interesting result thus emerges: there is an "interference" effect which causes the transition moments for processes B and C to be relatively small. Thus, although a large satellite may be observed in the XPS spectrum in the region of P_2 , the corresponding semi-Auger structure in the $P_1 \rightarrow P_2$ XES spectrum may be weak or unobservable.

A similar type of structure on the high-energy side of the diagram line (Process C) will also be diminished in intensity. The satellite-to-satellite transition (D) should have very nearly the same transition moment as the diagram line. Neglecting the energy-dependent factor in the XES cross section,¹⁴ the intensity of this transition relative to the main line A should then be given by the relative populations of the initial states. For the experimental situation of excitation by high-energy photons, this factor will be simply the relative intensity of S_1 to P_1 in the photoelectron spectrum. We note finally that the arguments presented above imply that the energies of the two transitions (A and D) should be very nearly the same, and the two peaks may be superimposed on one another and not readily resolved.

While an accurate description of real compounds will be more complicated than the simple model presented here, we believe that for those cases in which the XPS satellite structure can be understood in terms of a few strongly-interacting configurations, the general qualitative predictions of this model will be correct. We return to this point in connection with the "anomalous" x-ray spectra of transition-metal compounds in Section IV.

B. Core-Valence Transitions

The development in the preceding section is applicable to this situation as well. An important difference, however, is that the final-state hole is now in the valence shell, and one would not in general expect the dominant valence-electron excitations $k \rightarrow l$ and $m \rightarrow n$ to be identical. The XES satellite structure therefore becomes more similar to that observed in XPS, as shown below.

We consider again the four states defined in Equations (3)-(5), and note that when we assume the excited components $k \rightarrow \ell$ and $m \rightarrow n$ to be different, then the analogue of T' in Eq. (7b) is zero. A straightforward evaluation of the XES transition moments yields

$$\begin{aligned} I_A &\propto c_{01}^2 c_{01}^2 c_{02}^2 T^2 \\ I_B &\propto c_{01}^2 c_{01}^2 c_{12}^2 T^2 \\ I_C &\propto c_{11}^2 c_{11}^2 c_{02}^2 T^2 \\ I_D &\propto c_{11}^2 c_{11}^2 c_{12}^2 T^2 \end{aligned} \quad (8)$$

In these expressions the first factor comes from the initial state population; i.e., the fraction of $|P_1\rangle$ or $|S_1\rangle$ that consists of $|P_1^{FO}\rangle$. All coefficients are taken as real for simplicity. T is defined in Equation (7a). Taking ratios, we find

$$\begin{aligned} I_B/I_A &= c_{12}^2/c_{02}^2 \\ I_C/I_A &= c_{11}^4/c_{01}^4 \\ I_D/I_A &= (c_{11}^4/c_{01}^4) (c_{12}^2/c_{02}^2) \end{aligned} \quad (9)$$

Now c_{01}^2 and c_{02}^2 are of order unity, while c_{11}^2 and c_{12}^2 are typically very roughly an order of magnitude smaller. We see that the relative intensity of the semi-Auger process populating the state S_2 (path B) is the same as that predicted for the satellite intensity in the XPS transition to state S_2 . This comes about because the intensities of both transitions are effectively governed by the component of the frozen orbital configuration (P_2^{FO}) in the eigenstate S_2 . The intensities of

processes C and D are smaller, primarily due to the weighting by a small initial-state population.

The qualitative predictions of this simple model regarding the XPS and XES satellite intensities for the 3s region of argon are borne out by configuration interaction calculations described in the next section. This relationship is also examined for a number of experimental XPS and XES spectra in Section IV, but, due to rather large uncertainties in the relative intensities, it is not possible at this time to make definitive conclusions concerning the validity of the simplifications which lead to these predictions.

III. Argon XPS and XES Spectra

The 3s hole state of the argon atom is one of the classic examples of strong final-ionic-state configuration interaction (FISCI).^{15a} In hindsight, a clue to this behavior was provided as early as 1965 in Bagus' Δ SCF calculations on the argon atom.^{15b} Even with the inclusion of relaxation, Bagus found that the computed 3s binding energy was still ~ 4 eV above the experimental value. He furthermore noted that a simple consideration of pair correlation energies would predict the computed binding energy to be too low rather than too high. This implies that relative to the ground state there must be a strong stabilization mechanism for the final state in addition to orbital relaxation. Since that time, Luyken¹⁶ has shown that the experimental intensities of the lines in the Ar^+ optical spectrum deviate strongly from the predictions of a Hartree-Fock model; the theoretical intensities, however, change by as much as 100% with the

introduction of configuration interaction. Luyken's "parameterized" CI calculations established the important mixing as due to $3s^1 3p^6 ({}^2S)$ and $3s^2 3p^4 nd ({}^2S)$. A more direct experimental verification of this mixing is, of course, provided by the strong satellites observed in the 3s photoelectron and $L_{2,3}$ x-ray emission spectra.

Because of the availability of XPS and XES experimental data on argon, we chose this as a model case to test the ideas presented in Section II. The ab initio SCF and CI calculations are discussed in Section II-A, followed by a comparison with the experimental results in Section II-B.

A. SCF and CI Calculations

As discussed earlier, the most intense satellite structure in the XPS spectrum has been attributed to 2S states in Ar^+ ; an examination of Moore's Tables,¹⁷ however, shows that the region where intensity is observed (binding energies of ~37-41 eV) is also rather rich in states based on $3p^{-1} ({}^2P)$. In fact, from considerations of intensity variations as a function of photon energy, Spears, et al.¹⁸ assigned the first satellite in the XPS spectrum to the configuration $3s^2 3p^4 4p ({}^2P)$. Our calculations for the final states are therefore logically divided into those of 2P and 2S symmetry.

An extended basis set of Slater-type orbitals (STO's) optimized by Bagus^{15b} for the ground state of argon was used to obtain the " Δ SCF" binding energies and double ionization limits presented in Table I. In order to describe the satellites, additional Rydberg functions must be added to the basis set. There are 15 low-lying 2P states assigned

in the optical spectrum of Ar II, but only four of these states have the odd parity necessary for interaction with $3s^2 3p^5 (^2P)$. They involve the configurations $3s^2 3p^4 4p$ and $3s^2 3p^4 5p$, each of which gives rise to three linearly independent 2P functions. A single STO was chosen to represent each of the 4p and 5p orbitals by performing the pertinent 3x3 CI, and varying the exponent to minimize the energy of the lowest root of the matrix. In these optimizations, the SCF orbitals for the $3s^2 3p^4 (^1D)$ double ionization limit were used as a fixed core, and each additional STO was Schmidt-orthogonalized to the core and any lower-lying Rydberg functions of that symmetry. In other words, the 5p STO was orthogonal to both the core and the 4p STO optimized in a previous step. The optimum exponents obtained in this way ($\xi_{4p} = 0.90$, $\xi_{5p} = 0.60$) were found to be largely independent of the symmetry of the state and the orbitals used to define the core. For instance, similar optimizations of a 4p orbital for the 2S state of $3s^2 3p^4 4p$ and $3s^1 3p^5 4p$ both yield exponents in the range 0.85-0.90.

The functions representing Rydberg orbitals in the 2S states $3s^2 3p^4 nl$ were also chosen in this manner ($nl = 4s(1.15)$, $5s(0.70)$, $4p(0.9)$, $5p(0.6)$, $4d(0.6)$, $5d(0.52)$, $6d(0.35)$). Finally, because of its anticipated importance, the 3d function was found by optimizing a set of three 3d STO's which minimize the Hartree-Fock energy of $3s^2 3p^4 3d (^2S)$. The energies of the states found in this way are shown in Table II.

With the one-electron basis set chosen in this manner, configuration interaction calculations were performed for the ionic states; effective XPS satellite intensities were computed by evaluating the

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overlap between the frozen-orbital primary ionic state and the eigenvectors of the CI matrix. The configuration list used in our first calculation included the union of single replacements with respect to three reference configurations ($3s^2 3p^5$, $3s^2 3p^4 4p$, $3s^2 3p^4 5p$) in the case of the 2P states, or five reference configurations ($3s^1 3p^6$, $3s^2 3p^4 4s$, $3s^2 3p^4 4d$, $3s^2 3p^4 5s$) in the case of the 2S manifold. In these first model calculations, the virtual orbitals consisted of the Rydberg functions $3d$, $4s$, $4p$, $4d$, $4f$, $5s$, $5p$ and $5d$ as well as an additional set of three $3s$ and three $3p$ STO's chosen to have large amplitudes in the same spatial region as the $3s$ and $3p$ Hartree-Fock functions. This latter set of virtuals is appropriate for describing any orbital polarization in the $n = 3$ shell which may occur from state to state. The model thus includes configuration mixing in the various Rydberg "channels" as well as providing for orbital polarization within the core.^{17,19}

The final point that we wish to make in connection with the CI calculation is that the "union of single replacements" approach for the configuration list largely solved the problem of the choice of an appropriate set of occupied orbitals to describe the reference states. For example, we found that the energies of the CI roots which correspond to the five 2S reference configurations were independent, to within 0.2 eV, of whether we used the ground-state orbitals, the Hartree-Fock orbitals for the primary hole state ($3s^1 3p^6$) or the Hartree-Fock orbitals for the $3s^2 3p^4 ({}^1D)$ shake-off limit. The relative intensities were somewhat more sensitive to the choice of orbitals, as displayed in Table III, but in view of the model nature of the

calculations, they are satisfactorily independent of the choice of core orbitals (largest deviation ~3%). Because of the computational advantages associated with evaluating overlap integrals using the same one-electron basis for both the initial and final states, all further calculations utilized the ground-state orbitals to define the basis set. With regard to the $L_{2,3}$ x-ray emission intensities, the wavefunction for the initial state (2p hole-state) was again approximated by a configuration expansion utilizing the ground-state orbitals. In this case the configuration list included all single replacements with respect to the primary hole state, and thus the resulting wavefunction is roughly of Hartree-Fock quality. The energy computed for the 2p hole state was -517.6836 a.u., to be compared with the Hartree-Fock result of -517.6690 a.u.

B. Results and Discussion

The first conclusion to be drawn from our calculations is that the 2P satellites based on the 3p hole state can be safely disregarded when discussing the more intense satellite structure. The most intense were found to be the three 2P states based on $3s^2 3p^4 4p$, the strongest of these having an intensity of 0.8% that of the 3p primary ionic state and a separation of 7.3 eV from the 3s primary ionic state. Using the experimentally determined 3p/3s cross section ratio of 1.5 at AlK α energies,¹⁸ this predicts the 3p satellite to have an intensity of 1.2% that of the 3s primary hole state. Spears, et al.¹⁸ report a relative intensity of $3 \pm 2\%$. Our calculations on the 2S manifold also provide a source of intensity in this region of approximately 2.5% (relative to the 3s hole state) arising from the final state $3s^2 3p^4 4s(^2S)$.

Thus the calculations suggest that intensity in this region arises from both 2P and 2S final states. Before leaving this point, we note that the situation could be clarified by an examination of the $L_{2,3}$ x-ray emission spectrum since the 2P final states should not be observed as semi-Auger satellites while the 2S final states are allowed. The remainder of our discussion focusses on the 2S manifold.

The results for the 2S satellite intensities are reproduced along with the experimental results of Spears, et al.¹⁸ in the second and third columns of Table IV. A comparison shows that while the agreement is quite satisfactory for the first two states, the computed intensity for the $3s^2 3p^4 4d$ satellite is much too high. The reason for this behavior comes from the fact that there is a strong interaction not only between the primary hole state and the Rydberg channels, but also with the shake-off continuum based on $3s^2 3p^4 \epsilon d$. This behavior was surmised in the earlier work of Luyken¹⁶ and observed in calculations of photoionization cross sections.²⁰ In this work, it was studied by performing a series of CI calculations in which the size of the one-electron basis was systematically extended. We found that inclusion of a 6d Rydberg orbital in the original basis set did not significantly change the relative intensities; however, the addition of a single d orbital with $n = 3$, $\xi = 3.5$ reduces the relative intensity of the $3s^2 3p^4 4d$ satellite from 25% to 18%. Because this d function has a large amplitude in the valence region and is Schmidt-orthogonalized to the Rydberg orbitals, it has a large number of nodes and acts as a representation of a continuum function. The configuration representing the shake-off continuum $3s^2 3p^4 \epsilon d$ has a large matrix element with $3s^1 3p^6$,

which indirectly affects the admixture of $3s^1 3p^6$ in the root corresponding to the discrete satellite $3s^2 3p^4 d$. Our final results, shown in the fourth column of Table IV, have three additional d-type functions representing the continuum added to the original basis. Addition of the first continuum-like d function accounted for most of the change in intensity, but because conventional CI procedures are not very efficient ways of dealing with this type of effect, we can not be quite certain that we have essentially reached the one-electron basis limit for our admittedly restricted CI calculation. We tend to believe that the next major improvement in the wavefunctions would be achieved by adding to the types of electron distributions (e.g., double replacements with respect to the reference states) rather than expanding the one-electron basis.

Even though our description of the final state wavefunctions is only qualitative, there are some important features which bear mention. The first of these is that the total probability for multiple excitation increases dramatically when correlation is introduced into the 3s hole-state wavefunction. In the Hartree-Fock approximation for the final state, a total of 4% of all ionization events are predicted to go into multiple excitation. This increases by an order of magnitude when limited CI is introduced. This increase is also reflected in the computed binding energy. With respect to the Hartree-Fock initial state, the calculated value is 25.4 eV compared to the Δ SCF result of 33.2 eV. This additional 7 eV of "relaxation energy" accompanying the increase in multiple excitation probability is, of course, a computational manifestation of the sum rule.²¹ It is interesting to

note that when the continuum channels are included the major effect is a redistribution of the intensity in the various channels, rather than a large change in the total probability for multiple excitation; i.e., intensity is shifted from shake-up processes into shake-off channels.

One further investigation was performed with respect to the XPS satellite intensities, namely to consider the influence of a correlated initial state. Using our largest one-electron basis (Basis 2), we performed a CI calculation on the argon ground state which included all double replacements with respect to the SCF configuration. The energy was decreased to -527.0000 a.u. (implying a 3s binding energy of 30.4 eV; experiment gives 29.2 eV). The total probability for multiple excitation was increased only slightly to 39%, and the intensities of the individual channels were fairly insensitive to this improvement in the initial state. The intensities computed for satellites 2-5 were, respectively, 2.7%, 15.0%, 16.0%, and 0.6%. As stated earlier, we feel that the most significant improvement in the theoretical description will come about through inclusion of double replacements with respect to the reference states.

Turning now to the x-ray emission satellites, we see in Table IV that the agreement with experiment appears to be fairly satisfactory. There are two reasons for regarding this with suspicion, however. First of all, there are rather large uncertainties associated with the experimental intensity. The value in Table IV comes from a determination of the area of the peak using a planimeter and the spectrum published by Cooper and LaVilla.⁷ No discrete structure in the semi-Auger "peak" is resolved in their work, and although Werme, et al. resolve

a great deal of structure, we have no way of extracting even approximate intensities from their spectrum. The second consideration is that the theoretical intensity of the $3s^2 3p^4 4d$ satellite is undoubtedly inaccurate since the XPS results indicate we have done a relatively poor job of representing this state.

The most important point we wish to make is that the relative intensities calculated for the XES transitions are very nearly the same as in XPS. This provides some quantitative support for the assertion made in Section II that to a good approximation we need only consider the contribution to the transition moment from the component of the primary ionic configuration in each state, and, therefore, that a core $\rightarrow$ valence semi-Auger satellite should have approximately the same intensity as the corresponding XPS satellite.

IV. Discussion

The large mixing discussed for the argon 3s hole state is not unique to that case. A compilation of experimental information for the valence s levels of the third, fourth, and fifth rows of the Periodic Table is presented in Table V. This table includes data obtained from both solid and gas-phase species; some caution should therefore be exercised before interpreting trends (particularly across a given row) as solely "atomic" effects. The data on the inert gases show that the mean satellite separation decreases as one goes down a

column; this holds true for the other columns of the Periodic Table as well. The relative intensity of the structure, however, increases from Ar to Xe. We note that this behavior is predicted by the sum rule²¹ if the relaxation energy for the outermost s shell is roughly constant as one goes down the chart. This seems reasonable considering that in each case the s shell has the same number of electrons in "external" subshells (i.e., np^6). These "external" electrons provide by far the largest contribution to the relaxation energy.

Rough estimates of the intensities of the semi-Augur satellites in K^+ and Cl^- $L_{2,3}$ emission in KCl are available from Cooper and LaVilla's work. We estimate the structure to be ~20% ($\Delta E = 14$ eV) for K^+ and ~25% ($\Delta E = 6$ eV) for Cl^- . These intensities are qualitatively similar to those observed in the XPS data, and the energies are, as they should be, identical within the stated experimental errors.

The other principal contributor to satellite structure, multiplet splitting, can be distinguished from the satellites we have discussed in that the latter have the same symmetry as the primary hole state. Multiplet splitting is a "zeroth-order" effect compared to the "shake-up" satellites, and the intensity of a given L-S ionic state in XPS is given, to first order, by the square of the coefficient of fractional parentage of that (N-1) electron L-S coupling in the N-electron initial state. Thus the multiplet components will usually all be of different symmetry; a consequence of this being the XES transitions analogous to semi-Augur (within the multiplet manifolds) may be forbidden by the dipole selection rules. One would expect this possibility to occur most frequently in core-valence transitions.

Theoretical treatment of the intensities of the allowed XES transitions can be performed using the standard techniques of angular momentum theory,¹⁰ and it is not at all clear that the absence of satellites in XES implies a "shake-up" origin for them.¹¹ A much better method for distinguishing the two experimentally has been utilized by Carlson.²² His approach rests on the expected independence of "shake-up" intensities and energies with respect to the specific core-orbital. This is, of course, the basic assumption made in Section II of this paper.

We summarize this discussion of XES transitions in the form of a set of rules below. Again, we stress that we believe these should have qualitative significance; the extent of the quantitative relationships must await more detailed emission spectra.

1. Core-Core XES Transitions

If the XPS structure arises from an excited state of the same symmetry as the primary ionic state, no type B and C satellites should be observed in XES. Furthermore, the type D satellite should be very nearly equal in energy to the diagram line and may not be resolved from it.

This type of behavior has been noted and commented on by Asada, et al.¹⁰ in the $K\beta$ spectrum of NiF_2 . While there are intense satellites in the $Ni(2p)$ XPS spectrum, they are not observed in XES.

2. Core-Valence XES Transitions

In this case, the type B (semi-Augur) satellites should have nearly the same relative intensity as the pertinent "shake-up" structure

in XPS. The type C and D satellites should be weaker than the corresponding structure in XPS, primarily due to the reduced initial state population. We have already presented examples of type B satellites in the $L_{2,3}$ XES spectrum of Ar, K^+ , and Cl^- .

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TABLE I. SCF RESULTS FOR PRIMARY IONIC
STATES AND DOUBLE IONIZATION LIMITS

<u>State</u>	<u>Energy</u> ^a	
$3s^2 3p^6 (^1S)$	-526.8174	(0.0 eV)
$3s^2 3p^5 (^2P)$	-526.2738	(14.8 eV)
$3s^1 3p^6 (^2S)$	-525.5972	(33.2 eV)
$3s^2 3p^4 (^3P)$	-525.3025	(41.2 eV)
$3s^2 3p^4 (^1D)$	-525.2277	(43.3 eV)
$3s^2 3p^4 (^1S)$	-525.1165	(46.3 eV)
$3s^1 3p^5 (^3P)$	-524.5350	(62.1 eV)
$3s^1 3p^5 (^1P)$	-524.3930	(66.0 eV)

^a The Hartree-Fock energy in atomic units. Energies (in electron units) relative to the ground state of neutral argon are given parenthetically.

TABLE II. SCF RESULTS FOR EXCITED STATES IN ArII^a

State		Energy ^b	
$3s^2 3p^5$	(² P)	-526.274	(14.8)
$3s^2 3p^4 4p$	(² P)	-525.800	(27.7)
$3s^1 3p^6$	(² S)	-525.597	(33.2)
$3s^2 3p^4 3d$	(² S)	-525.521	(35.3)
$3s^2 3p^4 4p$	(² P)	-525.510	(35.6)
$3s^2 3p^4 4s$	(² S)	-525.495	(36.0)
$3s^2 3p^4 5p$	(² P)	-525.445	(37.3)
$3s^2 3p^4 4p$	(² P)	-525.400	(38.6)
$3s^2 3p^4 4d$	(² S)	-525.385	(39.0)
$3s^2 3p^4 5p$	(² P)	-525.375	(39.2)
$3s^2 3p^4 5s$	(² S)	-525.300	(41.3)
$3s^2 3p^4 5p$	(² P)	-525.265	(42.2)
$3s^2 3p^4 5d$	(² S)	-525.184	(44.4)
$3s^2 3p^4 6d$	(² S)	-525.148	(45.4)

^a Only the values for $3s^2 3p^5$ (²P), $3s^1 3p^6$ (²S), and $3s^2 3p^4 3d$ (²S) are of Hartree-Fock quality. The remaining entries result from optimizing a single Slater orbital in the field of a fixed core (see text).

^b Energy in Hartrees; the energy of each state relative to the Hartree-Fock energy for the argon ground state (in eV) is given parenthetically.

TABLE III. BASIS SET DEPENDENCES OF ARGON VALENCE-SHELL SATELLITE INTENSITIES^a

State	Energy (a.u.)			Intensity ^b		
	<u>A</u>	<u>B</u>	<u>C</u>	<u>A</u>	<u>B</u>	<u>C</u>
$3s^1 3p^6$	-525.809	-525.805	-525.810	100% (.592)	100% (.592)	100% (.604)
$3s^2 3p^4 4s$	-525.554	-525.557	-525.560	1.7	1.6	1.5
$3s^2 3p^4 3d$	-525.469	-525.417	-525.472	18.8	19.4	20.0
$3s^2 3p^4 4d$	-525.361	-525.364	-525.368	31.7	30.6	28.5
$3s^2 3p^4 5s$	-525.337	-525.342	-525.346	5.6	6.1	5.0

^aThe column headings A, B, and C refer to calculations using orbitals optimized for the ground state, the 3s hole state, and the $3s^2 3p^4(^1D)$ shake-off limit, respectively. The calculations were done with a one-electron basis of 7s, 6p, 2d, and 1f function.

^bThe absolute value of the overlap integral squared is given parenthetically.

TABLE IV. ARGON XPS AND XES SATELLITE INTENSITIES

Final State ^a	Exp. ^b	XPS (I_i/I_o) ^c		XES (I_i/I_o) ^f	
		Basis 1 ^d	Basis 2 ^e	Exp. ^g	Basis 2 ^h
3s ¹ 3p ⁶	100%	100% (0.60)	100% (0.63)	100% (219.2, 221.4 eV) ^j	100% (223.2 eV)
3s ² 3p ⁴ 4s	3 ± 2% (8.1 eV) ⁱ	1.8% (7.4 eV)	2.5% (8.8 eV)		3.6% (8.8)
3s ² 3p ⁴ 3d	17 ± 2% (9.4)	18.1% (9.5)	14.4% (10.4)		14.7% (10.4)
3s ² 3p ⁴ 4d	6 ± 3% (11.9)	25.4% (12.3)	15.1% (13.0)	35% (11 eV)	14.8% (13.0)
3s ² 3p ⁴ 5s	—	1.7% (13.3)	0.6% (14.8)		0.5% (14.8)

^a Although the calculations predicted intensity in other roots as well (most notably 3s²3p⁴5d), we list only those reference states which the calculation was specifically designed to treat semi-quantitatively.

^b Ref. 18; an average of AlK α and MgK α excited spectra.

^c The satellite intensity relative to the primary ionic state. The first entry in the theoretical columns gives the square of the absolute overlap in the primary ionic state; for the other states the parenthetical entry is the energetic separation from the primary ionic state, in eV.

^d Basis 1 contained Rydberg d-channels but no "continuum" d functions (see text). The absolute energy of state 1 is -525.8271 a.u.

^e Basis 2 contained, in addition to those orbitals in Basis 1, three d STO's (n = 3, ξ = 3.5; n = 3, ξ = 2.5; n = 4, ξ = 2.2). The absolute energy of state 1 is -525.8845 a.u.

^f The satellite intensity relative to the L_{2,3} diagram line. All transition moments were evaluated in the length form, i.e., $I_i/I_o = \frac{E_o^3}{E_i^3} \frac{|T_i|^2}{|T_o|^2}$, where $T = \langle \psi_{\text{final}} | \vec{r} | \psi_{\text{initial}} \rangle$, and E is the transition energy.

TABLE IV. (Continued)

^gRef. 7; we have crudely estimated the intensity from their published spectrum. Although Werme, et al. subsequently published a much higher resolution spectrum, we have no way of estimating intensities from their spectrum.

^hThe calculated x-ray energy is given parenthetically.

ⁱThere is also a contribution to the intensity in this region from a 2P satellite; see text.

^jThe two spin orbit terms from Ref. 7.

Table V. XPS Correlation Satellite Separations (eV)^{a,b,c}

n1 = 3s	(S ⁻²)-	(Cl ⁻) 6 ^{c,d,e,f}	(Ar) 11(25%) ^g	(K ⁺) 14 ^{c,d,f,g}	(Ca ⁺²) 16 ⁱ
4s	(Se ⁻²)-	(Br ⁻) 4 ^c	(Kr) 6.5(30%) ^g	(Rb ⁺) 11 ^{f,g}	(Sr ⁺²) 13.5 ^{c,i}
5s	(Te ⁻²)-	(I ⁻) 3.6 ^c	(Xe) 6.0(58%) ^{g,h}	(Cs ⁺) 9.3 ^{g,h}	(Ba ⁺²) 9.9 ^{h,i}

^aWith the exception of the rare gases, the entries in this table are taken from XPS measurements of appropriate salts. In those cases where a given ion has been studied in several salts (e.g., K⁺ in KF, KCl, and KBr), the satellite separation is an average of the observed separations. In most instances, the deviations from salt to salt are within the experimental uncertainty in the separations (~.2 eV).

^bParenthetical entries for the rare gases are the relative intensity of the correlation satellite to the primary peak.

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FIGURE CAPTION

Fig. 1. A hypothetical ionic state diagram. The states labeled P_1 and P_2 are two of the primary ionic states of the system; associated with each of them is a satellite state, S_1 or S_2 . The x-ray emission transition labeled A produces the diagram line, while B corresponds to a semi-Auger peak. Processes C and D are similar, but originate from decay of the satellite state S_1 .

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Fig. 1

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