Molecular-Orbital Model for the Chemical Effect on the K-X-Ray Spectrum of Fluorine

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A new model based on the linear combination of atomic orbitals molecular-orbital wave functions is proposed to explain the reduction of the relative intensity of the fluorine KL^1 satellite line in covalent fluorine compounds. Values of a reduction factor r of the KL^1 line intensity are calculated and compared with experimental ones. Agreement is found for the size of the factor, but problems are found in use of the Pauling crystal ionicity to characterize molecular orbits. In addition, it is shown that the same effects are expected for direct and shakeoff multiple ionization in application of the sudden-approximation method to molecular wave functions.

In recent years the effect of chemical environment on the relative intensity of K-x-ray satellites produced by heavy-ion bombardment was studied for many elements. A review of all these measurements is given by Raman and Vane.[1] The largest effects are found for the KL^1 satellite line of fluorine, where the L shell is the valence shell.[2] For the highly ionic alkali and alkaline-earth fluorides a resonant electron transfer was found[3] to explain the abnormally low intensity of the KL^1 peak for KF and SrF_2. Covalent fluorine compounds were studied in a series of investigations by Uda and co-workers.[4-6] They found that the energy of KL^1 x rays is insensitive to change of the chemical environment, but that the relative intensity of the KL^1 line is strongly correlated with the ionicity of the compounds on the Pauling ionicity scale. However, as yet no detailed model capable of explaining the cause of this change of relative intensity of the KL^1 line is available for making a quantitative evaluation of this effect.

In this work we propose a new model to explain the KL^1 intensity reduction, based on the linear combination of atomic orbitals (LCAO) molecular-orbital wave functions. Within this model a quantitative calculation of the reduction factor is also possible. Comparison with experimental reduction factors for different fluorine compounds gives good agreement in the range of expected values; however, using the Pauling ionicity for crystals to calculate properties of molecular orbits, we found large discrepancies indicating uncertainty of ionicity scales. In addition, we show that x-ray spectra excited by photons or electrons and by ion impact give about the same reduction factor as experimentally found. To prove this, shakeoff probabilities are calculated by the sudden-approximation method for molecular-orbit electrons.

The ionization cross section for multiple ionization of one K and n L electrons can be expressed by

$$\sigma_{KL^n} = 2\pi \int_0^\infty P_K(b) P_{L^n}(b) b \, db, \tag{1}$$

where $P_K(b)$ and $P_{L^n}(b)$ are the probabilities that an

incoming ion with impact parameter b ejects one K and n L electrons, respectively, for independent K and L ionization. On the assumption that $P_K(b) = 0$ for $r > r_K$, where r_K is an effective K-shell radius, and $P_{L^n}(b) = P_{L^n}(0)$ for $b < r_K$, Eq. (1) simplifies to

$$\sigma_{KL^n} = \sigma_K P_{L^n}(0), \tag{2}$$

where σ_K is now the total K-shell ionization cross section. The probability that when a K electron is ejected, n additional L electrons are also ejected is

$$P_{L^n} = \sigma_{KL^n}/\sigma_K = P_{L^n}(0). \tag{3}$$

There are calculations[7-10] of P_{L^n} evaluated directly from Eq. (1) or the approximation $P_{L^n}(0)$ by use of theories formulated in terms of the impact parameter, e.g., the binary-encounter approximation or the semiclassical approximation theories. So far, only atomic wave functions have been used in these calculations. However, for solid targets of elements or compounds of elements with atomic number $Z < 10$, in which the L shell is the valence shell, covalent bondings may cause large deviations in P_{L^n} from those calculated with atomic wave functions.

To take the effect of covalent bonds into account, let us consider first an atom A with one L or valence electron forming with an atom B a pair molecular-orbit (MO) bond in the LCAO model. The MO wave functions should be

$$\psi_1 = a^{1/2}\phi_a + (1-a)^{1/2}\phi_b,$$
$$\psi_2 = (1-a)^{1/2}\phi_a + a^{1/2}\phi_b, \tag{4}$$

with $0 \le a \le 1$ and $\langle \phi_a | \phi_a \rangle = 1$, $\langle \phi_b | \phi_b \rangle = 1$, where ϕ_a and ϕ_b are the atomic L-shell wave functions of the atoms A and B. A possible overlap of the atomic wave functions is neglected.

Consider now multiple ionization by ejection of one K electron on atom A and a ψ_1 MO electron. On the assumption that the ionization probability is proportional to the electron density at atom A, the probability

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is, according to basic theories, e.g., the binary-encounter approximation theory,[7]

$$P_{M1} = C \int_0^R \psi_1^*(r_a) \psi_1(r_a) \, dr_a, \tag{5}$$

where C is a constant, r_a is the electron distance from nucleus A, and R an effective atomic radius of atom A. The substitution of the LCAO wave function, Eq. (4), into Eq. (5) gives

$$P_{M1} = aC \int_0^R \phi^*(r_a) \phi(r_a) \, dr = aP_A, \tag{5'}$$

when P_A is the atomic $P_L(0)$ value. The corresponding ionization probability for ψ_2 is then

$$P_{M2} = (1-a)P_A. \tag{5''}$$

The probability of ejecting no additional L or valence (V)-shell electron, when a K electron is ejected, is now

$$N_M = (1 - P_{M1})(1 - P_{M2}) = 1 - P_A + a(1-a)(P_A)^2$$
$$= N_A + a(1-a)(P_A)^2. \tag{6}$$

As N_A is the atomic probability to eject no L electron for K ionization of atom A, we see that the single K ionization probability evaluated with MO's is increased, even though the total density of L or V electrons at atom A is not changed.

To evaluate the probability of multiple K and V ionization by photon or electron impact, we apply the sudden-approximation method[11] to LCAO molecular orbits. If ϕ_a' is the relaxed atomic wave function when a K hole is present, the probability that the ϕ_a electron is not ionized is

$$N_A = |\langle \phi_a' | \phi_a \rangle|^2. \tag{7}$$

If we now approximate a relaxed MO wave function by

$$\psi_1' = a^{1/2} \phi_a' + (1-a)^{1/2} \phi_b, \tag{8}$$

the equivalent nonionization probability is

$$N_{M1} = |\langle \psi_1' | \psi_1 \rangle|^2. \tag{9}$$

Substituting Eq. (4) and Eq. (8) into Eq. (9) gives

$$N_{M1} = |a\sqrt{N_A} + (1-a)|^2. \tag{10}$$

For comparison with Eq. (6), Eq. (10) can be written as a series in $1 - N_A$:

$$N_{M1} = 1 - a(1 - N_A)$$
$$- 0.25a(1-a)(1-N_A)^2 + \dots. \tag{11}$$

For $a < 0.5$ and $N_A < 0.5$, the third term in Eq. (11) gives only a small correction, and the ionization probability for a molecular orbital is in first approximation

$$P_{M1} = 1 - N_{M1} = aP_A.$$

This result is the same as for direct multiple ionization. Hence, because the primary ionization probabilities for different MO's are changing in the same way for shakeoff and for direct multiple ionization, the same effects of MO bonds on the intensity of the first KL^1 satellite line can be expected.

The energy shift $\Delta E(n)$ between the nth satellite line $E(KL^n)$ and the diagram line $E(KL^0)$ is found[12,13] to be roughly proportional to n,

$$\Delta E(n) = E(KL^n) - E(KL^0) = n\delta E,$$

where δE is the energy shift caused by one L vacancy. Thus for x rays from multiple K and ψ_1 MO ionized states, an energy shift of $a\delta E$ is now expected. But, as already mentioned, no shift of the energy of satellite lines due to the chemical environment is observed experimentally.[6] The first satellite line always has the same energy as the atomic or ionic KL^1 line; only the relative intensity is in general decreased. Accepting this observation, we propose as a next step in our model that ionization of one MO results in a break of the other MO. So, if ψ_1 is ionized, ψ_2 will break off and the ψ_2 electron will be located at either atom A or B. Before the break of the MO ψ_2, the probability of finding an electron at any time at atom A or B is $1-a$ or a, respectively. After the break, we assume the same probabilities $1-a$ and a that the electron is located on atom A or B. So, if for the MO there is a probability a of finding the MO electron at atom A, there is also the probability a, that the vacancy is located at atom A after ionization of this MO.

For multiple K and V ionization, localization of the MO vacancy at atom A will give rise to a satellite KL^1 transition, while localization at atom B will result in a normal diagram transition KL^0. Thus the intensity of the KL^0 line is now the sum of primary single K ionization and multiple K-V ionization, when the MO vacancy is not located at the atom A. The total intensity of the KL^0 line is therefore

$$I(KL^0) = N_{M1}N_{M2} + (1-a)P_{M1}N_{M2} + aN_{M1}P_{M2}, \tag{12}$$

where $N_{M1} = 1 - P_{M1}$ and $N_{M2} = 1 - P_{M2}$ are the MO nonionization probabilities. Substituting Eq. (5) into Eq. (12) results in

$$I(KL^0) = 1 - (1 - 2a + 2a^2)P_A.$$

The corresponding equation for $I(KL^1)$ is

$$I(KL^1) = aP_{M1}N_{M2} + (1-a)N_{M1}P_{M2} + P_{M1}P_{M2}, \tag{12'}$$

and substituting Eq. (5) results in

$$I(KL^1) = (1 - 2a + 2a^2)P_A.$$

From these expressions the relative KL^1 intensity R_{10} is

$$R_{10}(a) = I(KL^1)/I(KL^0),$$

and the reduction factor $r(a) = R_{10}(a)/R_{10}(1)$ can be calculated giving

$$r(a) = \frac{(1 - 2a + 2a^2)(1 - P_A)}{1 - (1 - 2a + 2a^2)P_A}. \tag{13}$$

This reduction factor for a pair MO bond is shown in Fig. 1 for different values of P_A. As can be seen $r(a)$ is almost independent of P_A for small values of P_A.

So far this model is valid only for one-valence-electron atoms, but a simple generalization to more L electrons can easily be performed. In order to apply the model to fluorine compounds, we took eight L electrons into account which form with eight other neighboring-atom electrons sixteen MO's, i.e., eight orbits of type ψ_1 and eight orbits of the type ψ_2. For each orbit we used the ionization and nonionization probabilities given by Eq. (5). The nonionization probability corresponding to Eq. (6) becomes

$$N_M = (N_{M1})^8 (N_{M2})^8.$$

Individual MO ionization probabilities were calculated on assumption of independent ionization of each MO. So for example, the probability of ionizing one ψ_1 and one ψ_2 MO is

$$P_{M1,M2} = 64 P_{M1}(N_{M1})^7 P_{M2}(N_{M2})^7.$$

In order to compare the model with experimentally observed reduction factors r of the first satellite line, small values of the individual P_A's were taken and ionization up to two MO's were considered. After ionization of a MO, breaking of the bonds was assumed since almost no shift of the energy of the KL^1 line is

found experimentally.[6] The localization probability of a MO vacancy at the F atom was taken to be, according to the single pair-bond MO model, the probability of finding the MO electron before ionization at the F atom. In this way intensities $I(KL^0)$, $I(KL^1)$, and $I(KL^2)$ were calculated for different a values. The resulting reduction factor $r(a)$ is shown in Fig. 2 for $P_A = 0.1$. This P_A value gives for $a = 1$ a satellite distribution with relative KL^1 intensity R_{10} of 0.89 which is close to experimental values for light-ion–induced ionization.[5] As can be seen, the dependence on a is almost the same as in Fig. 1, and again $r(a)$ is almost independent of P_A for $P_A < 0.15$.

As the reduction factor r is experimentally found to correlate with the ionicity of the individual compounds, we tried to find a relation between the LCAO parameter a and the ionicity. As pointed out by Phillips[14] and recently by Catlow and Stoneham,[15] ionicity is not a well-defined value, but more of a scale for comparing different compounds. We took the Pauling ionicity for crystals,[16] and not the molecular single-bond ionicity which gives much lower ionicity values. By use of a relation between the ionicity f and a polarity α_p, which is close to the parameter a given by Harrison[17] for a bond orbital model, there results

$$f = 1 - [4a^2(1 - a^2)]^{1.5}.$$

Figure 2 shows the experimental reduction factors[6] as a function of a together with the theoretical $r(a)$. [For $(CH_2)_n$ we used the normal Pauling bond ionicity.] The experimental reduction factors are about the same as the theoretical ones, but the calculated a values are too large. Here we want to point out that in Fig. 2 there are no free parameters. Although the theoretical model with use of eight equivalent valence
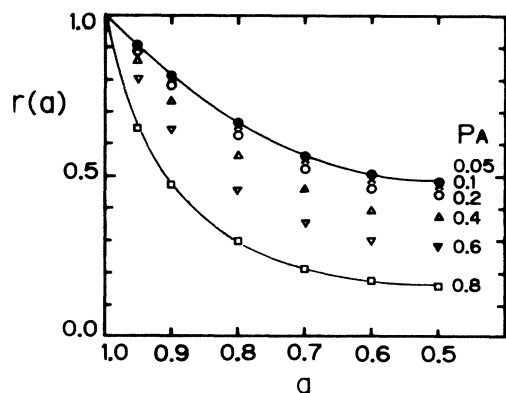

FIG. 1. The reduction factor $r(a)$ of the KL^1 satellite line calculated in the single pair-bond MO model as a function of the localization parameter a for different atomic L-shell electron-ionization probabilities P_A.
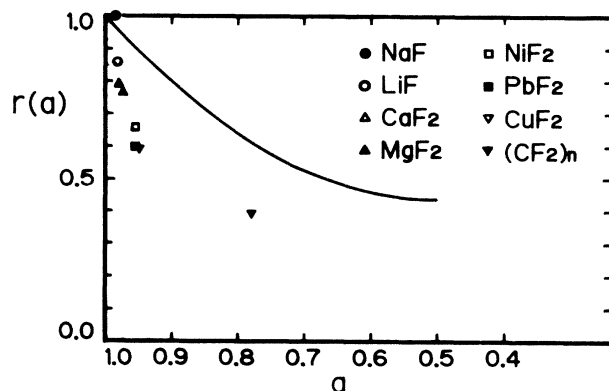

FIG. 2. The solid line is the reduction factor $r(a)$ resulting from the MO model for eight valence electrons and an ionization probability $P_A = 0.1$. The points are experimental results from Ref. 6. For calculation of the a values, Pauling's ionicity for crystals was used, while for $(CF_2)_n$ the normal bond ionicity was used.

electrons might be too simple, the large discrepancy indicates that the Pauling ionicity for crystals is not adequate to describe the localization of fluorine valence electrons in fluorine compounds. Additional delocalization due to overlap of fluorine $2p$ wave functions with neighboring fluorine $2p$ or metal inner-shell wave functions might be important. As a result of this analysis, the value of the localization parameter a for the compounds shown in Fig. 2 are expected to be between 0.75 and 0.92 [except for $(CH_2)_n$], according to Fig. 2.

In conclusion, we propose a new model for the chemical effect on the relative intensity of the KL^1 satellite line. It is shown that for multiple ionization induced by ion impact and by shakeoff the same effects are to be expected. Within the molecular-orbital model a reduction factor r of the intensity of the KL^1 satellite line is calculated as a function of the LCAO parameter a describing the localization of molecular orbits. Comparison with experimental values for fluorine yields agreement with reduction ratios, but discrepancies are found for the values of the equivalent localization parameter a calculated from ionicities, indicating problems with trying to describe localization of molecular wave functions by ionicity scales. The relative intensity of the KL^1 satellite line can be used to measure the localization of valence electrons at the atom where the K shell is ionized. This localization is an important factor for understanding bonds in molecules or solids and is difficult to determine by other experimental methods. Further calculations taking a larger number of different MO's into account are in progress.

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