Many-Electron Effects in the Shape of the Cl $K\alpha_{1,2}$ X-Ray Emission Lines

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Fluorescent Cl $K\alpha$ x-ray spectra were observed with a double-crystal spectrometer. $K\alpha$ line shapes appeared asymmetrically smeared by the presence of the shakeoff satellites within the natural width of main lines. Bonding effects of $KM^n \rightarrow LM^n$ satellites—parasites—of chlorine were observed ($n = 1, 2$) for the first time. The relative intensities of parasites were measured in a number of chlorine compounds. Except for RbCl and CsCl, the relative intensities were found to be related to the covalency of the compounds.

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Shapes of $K\alpha$ x-ray emission lines are usually interpreted as a sum of two Lorentzian functions ($1s^{-1} \rightarrow 2p_{1/2}^{-1}$ and $1s^{-1} \rightarrow 2p_{3/2}^{-1}$) provided that the x ray is emitted from the inner shells of diamagnetic insulators. However, shakeoff of valence electrons due to the photoionization of one $1s$ electron leads to the appearance of Wentzel-Druyvesteyn–type satellites[1] within the natural width of parent lines. Contamination by linewidth satellites causes asymmetrical smearing of the parent lines. This class of satellite was named *parasite*.[2] Many-electron effects, such as shakeoff processes, involving these valence electrons are affected by the chemical environment. Although chemical effects of well-separated satellites, $K\alpha'\alpha_{3/4}$, of oxygen or fluorine compounds were studied by many authors,[3–16] the only published report of chemical effects upon the linewidth satellites concerns potassium compounds.[17] The chemical effects of chlorine compounds are more striking than those of potassium compounds. This is not only because the $3p$ orbitals form valence bonds but also because there is a rather large range of chemical states from Cl^- (KCl) to Cl^{7+} ($KClO_4$) as a formal charge. As a result of the present work, the line shapes of x-ray emission spectra are recognized as a source of information of chemical state and electronic structure.

Figure 1 shows the observed and processed Cl $K\alpha$ x-ray emission spectra ($1s^{-1} \rightarrow 2p^{-1}$) of (a) sodium chloride and (b) *p*-chlorobenzoic acid. The experimental conditions for the present study were similar to those of previous reports.[17,18] We can therefore affirm that the parasites are observable with the present experimental conditions. A Toshiba AFV-701 two-crystal spectrometer[19] was used to measure the spectra. The Cr-target x-ray tube was equipped for primary excitation. Analyzer crystals were Si(111) + Si(111) with (+, +) arrangement. Measured spectra were smoothed by spline functions[20,21] and then deconvoluted with the natural width (0.72-eV Lorentzian[22]), using a modified van Cittert method.[23] The solid-line spectra in Fig. 1, therefore, contain the convolution of the spectrometer window and the δ functions of the x-ray transition energy levels.

Three compounds (C, D, E in Fig. 1) can be seen in the processed spectrum of Cl $K\alpha$ for NaCl, which resembles the Ar $K\beta$ spectra observed by Deslattes *et al.*[24] with respect to the three peaks. With assumption of a parallel relation between the $K\alpha$ and $K\beta$ spectra,[25] component D in Fig. 1(a) is the transition $KM \rightarrow LM$, and component E the transition $KM^2 \rightarrow LM^2$. This is because the Ar $K\beta$ satellites[24] were reassigned by Dyall and Grant[26] as $K\beta^v$ to $KM \rightarrow M^2$ and $K\beta''$ to $KM^2 \rightarrow M^3$. Parasite structure B, which may be the combination of the KM and KM^2 parasite structures of $K\alpha_2$, is also observed in Fig. 1(a). From an atomic $X\alpha$[27] calculation by means of Slater's transition-state method,[28] the energy of the $KM \rightarrow LM$ parasites shifts to a level 0.29–0.34 eV higher than the main line, and the $KM^2 \rightarrow LM^2$ parasites to a level 0.75–0.89 eV higher. Therefore the above parallel assignment of D and E in Fig. 1(a) is consistent with calculation. The spectrum of *p*-

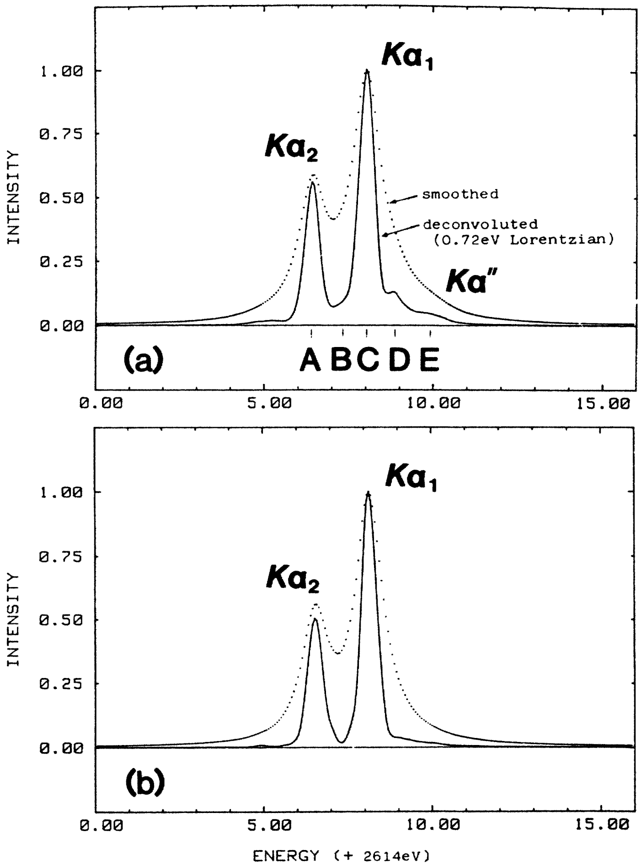

FIG. 1. Fluorescent Cl $K\alpha$ spectra of (a) sodium chloride and (b) *p*-chlorobenzoic acid. The observed spectra were smoothed with a spline function (dotted line) and then processed by deconvolution with the 0.72-eV Lorentzian function (solid line).

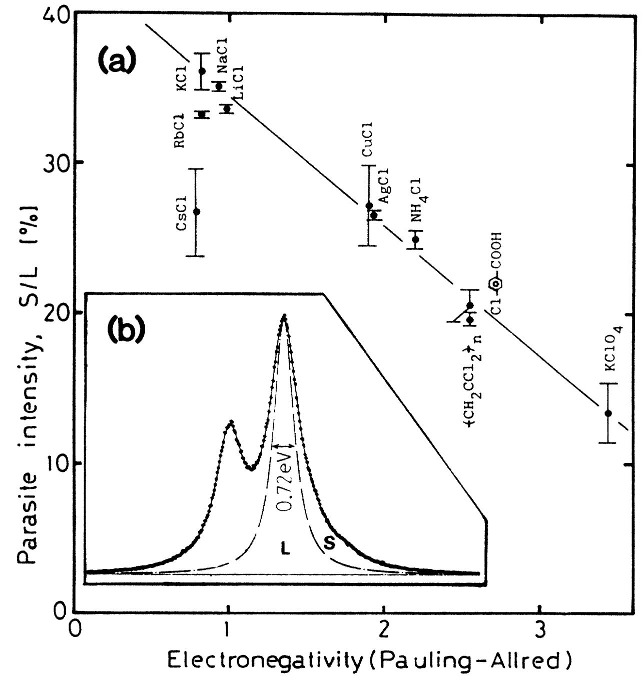

FIG. 2. (a) The parasite intensities S/L plotted as a function of electronegativity of the nearest-neighbor atom. Error bars indicate standard deviations of several measurements. (b) The definition of the parameter S/L. L is the area of the Lorentzian function of 0.72-eV FWHM, and S is the area of the high-energy shoulder of the $K\alpha_1$ line shape.

chlorobenzoic acid, which is more covalent than sodium chloride, has almost no parasite structure as far as can be seen in the deconvoluted spectrum of Fig. 1(b). However, if we introduce a new parameter of parasite intensity, S/L (see below), we find that the parasite intensity of *p*-chlorobenzoic acid is higher than that of $KClO_4$. Although this type of chemical effect has been observed for Cl $K\beta$ spectra,[29-31] this is the first report to present the chemical effects for Cl $K\alpha$ spectra.[32]

Figure 2(a) shows the relation of parasite intensity, S/L, to the chemical state, which is represented by the electronegativity[33] of the neighbor atom to the chlorine atom in the compounds; S/L is defined in Fig. 2(b). The solid line in Fig. 2(a), connecting KCl to $KClO_4$, is to guide the reader's eye. The parasite intensity shows a clear relation to the covalency of each compound, except for the cases of RbCl and CsCl. That is to say, the more covalent the bond, the weaker are the parasites. This ordering relation is the same as that reported for F KL satellites by Uda and coworkers.[10,11,16]

Having described the experimental results, let us now turn to interpretations of the following two points from a calculation by the cluster discrete-variational $X\alpha$ method[34]: (i) the reason why the parasite intensity is closely related to the bond covalency; and (ii) the reason why CsCl and RbCl are exceptions of (i).

(i) We calculated the relaxation energy of the Cl $3p$ orbital for the compounds of LiCl, NaCl, KCl, RbCl, CsCl, AgCl, PhCl (Ph denotes phenyl), and $ClO_4{}^-$, and found that if the relaxation energy of the Cl $3p$ orbital is large, then the parasite intensity is high, and vice versa. Here the calculated relaxation energy of the Cl $3p$ orbital, which is represented by the difference of Cl $3p$ orbital eigenvalues from the ground state to the Cl $1s^{-1}$ hole state, is 11.2 eV for LiCl (t_{1u}), 11.4 eV for NaCl (t_{1u}), 11.6 eV for KCl (t_{1u}), 10.6–12.6 eV for RbCl (t_{1u}), 10.8–12.3 eV for CsCl (t_{1u}), 9.7 eV for AgCl (t_{1u}), 10.6 eV for PhCl (b_2), and 8.9 eV for ClO_4^- (t_2). This implies that if the Cl $3p$ electrons are localized when the bond is ionic, then the orbital relaxation is large. Thus, the overlap integral $|\langle Cl\,3p|Cl\,3p^*\rangle|$ is small (the asterisk denotes

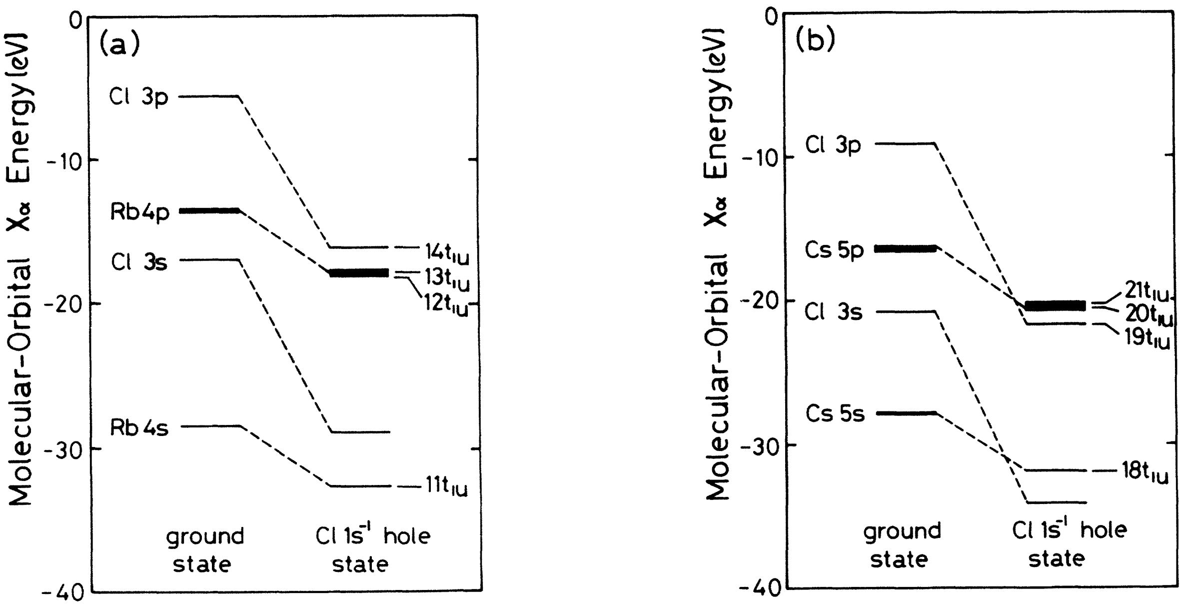

FIG. 3. Molecular-orbital discrete-variational-$X\alpha$ energy-level diagram of (a) $[\mathrm{ClRb_6}]^{5+}$ and (b) $[\mathrm{ClCs_8}]^{7+}$ for the ground state and for the Cl $1s^{-1}$ hole state.

the Cl $1s^{-1}$ hole state), and therefore the shakeoff probability, $6(1-\langle \mathrm{Cl}\,3p|\mathrm{Cl}\,3p^{*}\rangle^{2})/\langle \mathrm{Cl}\,3p|\mathrm{Cl}\,3p^{*}\rangle^{2}$, in the sudden approximation[29] is large. Therefore the intensity of $3p$ shakeoff satellites (parasites) of ionic compounds is a strong as that of the Cl^- free ion. On the other hand, if the bond is covalent, then the Cl $3p$ electron is delocalized, and thus the relaxation due to the core hole is small; therefore $\langle \mathrm{Cl}\,3p|\mathrm{Cl}\,3p^{*}\rangle^{2}\simeq 1$, and as a result the parasite intensity is low.

(ii) As mentioned in (i), the relaxation energies for CsCl and RbCl are somewhat wide ranged (10.6–12.6 eV for RbCl and 10.8–12.3 eV for CsCl). This is because there exist molecular-orbital splittings of incidentally degenerate levels between the Cl $3p$ atomic orbital and the ligands' orbitals. That is to say the orbital energy of Cl $3p$ is quite close to that of Rb $4p$ or Cs $5p$ in the RbCl or CsCl compounds, respectively, in the presence of a Cl $1s^{-1}$ hole (see Fig. 3). This means that a strong molecular orbital forms between Cl $3p$ and either Rb $4p$ or Cs $5p$ at the Cl $1s^{-1}$ hole state in spite of the fact that these two compounds are ionic in the ground state. The Cl $3p^{-1}$ holes are therefore resonantly transferred or delocalized through these molecular orbitals from Cl to Rb or to Cs,[35] as proposed by Benka, Watson, and Kenefic[12] and by Urch[13] for F $K\alpha$ satellite spectra. Therefore the parasites for RbCl and CsCl are weak.

In summary, experimental evidence has been presented that the $K\alpha$ line profiles are asymmetrically broadened as a result of shakeoff processes even in diamagnetic insulators, and that the parasite intensity is closely related to the ionicity of the compounds. We interpreted the chemical effect of line shapes, including the two cases (RbCl and CsCl); if we consider the covalency of the Cl $1s$ hole state, then the more delocalized the Cl $3p$ electron, the weaker the parasites become. On this basis, we conclude that this chemical effect is a measure of the delocalizability of the chlorine $3p$ electron in the compounds.

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