

## The Temporary Covalence of Potassium Fluoride (in X-Ray and Auger Spectra Processes)

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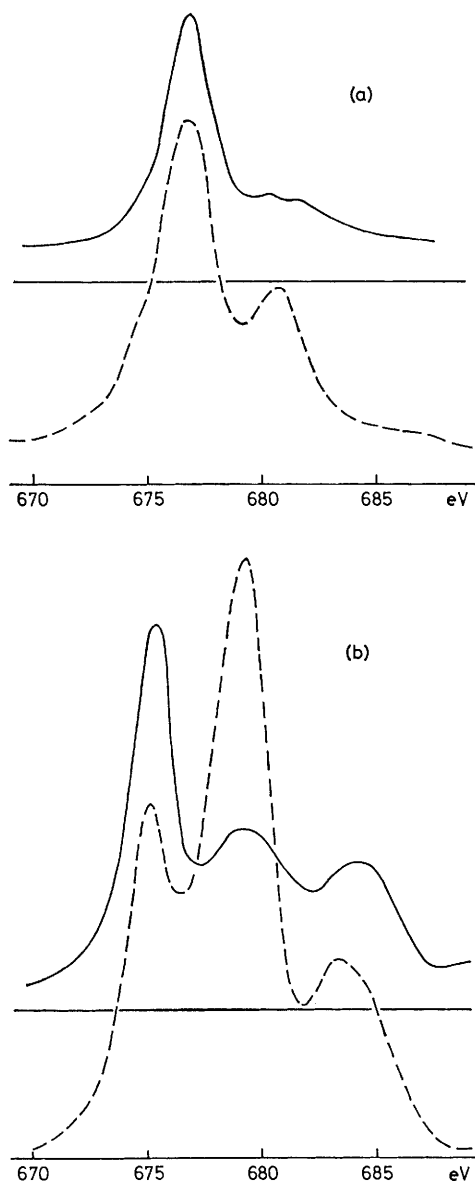
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The similarity in ionisation energy of  $K^+$  (3p) and of the second 2p electron from  $F^-$  enables molecular orbitals to be formed between doubly ionised fluoride and the surrounding potassium ions in potassium fluoride; this transitory covalency causes peak splitting in Auger spectra, and attenuation of high-energy satellite intensity in X-ray spectra.

X-Ray emission results from electronic relaxation in a singly ionised atom. When similar relaxation takes place in a multiply ionised atom 'satellite' peaks of higher energy than the main peak result. The most prominent are those from atoms with two vacancies, *e.g.*,  $1s^{-1}2p^{-1} \rightarrow 2p^{-2}$ ,  $K\alpha_{3,4}$ . Chemical effects both in the relative intensities of the constituent satellite peaks<sup>1</sup> and in the satellite peaks: main peak ratio ( $R$ )<sup>2-4</sup> have been observed. Uda and his co-workers<sup>2</sup> have recently investigated a series of fluorides and suggested that  $R$  may be used as an index of covalent character since  $R$  was found to decrease in the series NaF,  $MgF_2$ ,  $AlF_3$ , Teflon. However, in

more extensive investigations both Esmail<sup>3</sup> (X-irradiation) and Deconninck<sup>4</sup> (ion bombardment) have found very low values of  $R$  for potassium fluoride (Figure 1) (0.22<sup>3</sup>, 0.90<sup>4</sup>) and  $R$  values for caesium fluoride (0.35<sup>3</sup>, 0.98<sup>4</sup>) less than for sodium fluoride (0.49<sup>3</sup>, 1.23<sup>4</sup>). Using Uda's correlation potassium fluoride should be one of the most covalent compounds!

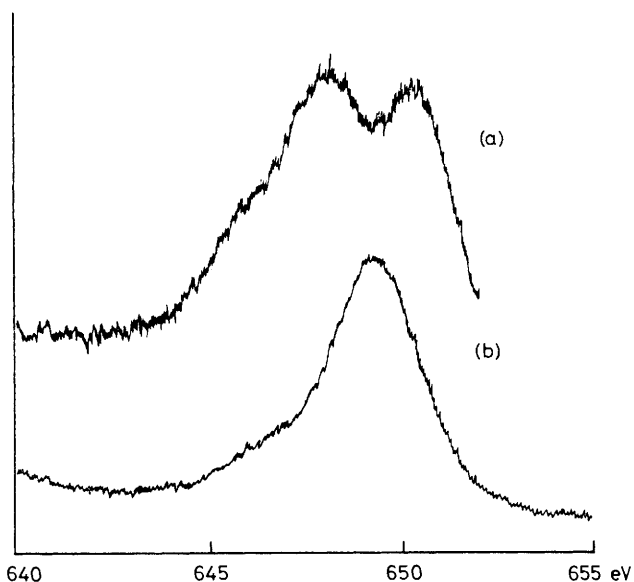
Since the Auger process can leave atoms in the same electronic final state as can high-energy satellite X-ray emission, Auger spectra might be expected to show features that could be related to X-ray satellite spectra. For potassium fluoride the fluorine Auger peak (KLL,  $2p^{-2}$ ) was found to be



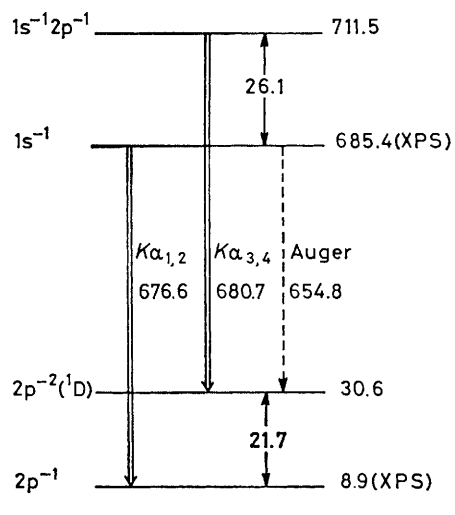
**Figure 1.** Fluorine  $K\alpha$  emission spectra from potassium fluoride (solid line) and sodium fluoride (dashed line) using (a) X-irradiation (3 kw Cr-anode) and (b) 2 MeV  $\alpha$ -particle bombardment.<sup>4</sup>

split into two peaks of almost equal intensity, separated by 2.3 eV (Figure 2). However, the total intensity of these peaks (by area) relative to the  $F^{-} 1s$  photoelectron peak was very similar to the intensity ratio,  ${}^1S + {}^1D$  Auger:  $F^{-} 1s$ , for sodium fluoride.

Thus in both X-ray and Auger spectroscopy potassium fluoride exhibits curious, anomalous behaviour. Data from X-ray emission, X-ray photoelectron, and Auger spectra enable an energy-level diagram for singly and multiply ionised states of the fluoride anion to be constructed (Figure 3). It is possibly significant that the ionisation energy of the second 2p electron from the fluoride anion (*i.e.* for  $2p^{-1} \rightarrow 2p^{-2}$ ) is only slightly greater than that of a 3p electron from the potassium cation (17.8 eV). This similarity in ionisation energies suggests that in a system such as  $(K^{+})_6F^{-}(2p^{-1})$  there could exist molecular orbitals involving both potassium 3p and fluorine 2p orbitals. Indeed the proximity of an  $F^0$  rather than  $F^{-}$  will enhance the ionisation energy of the potassium 3p



**Figure 2.** Fluorine  $2p^{-2}$  ( $K L_{2,3} L_{2,3}$ ) Auger electron spectra from (a) potassium fluoride and (b) sodium fluoride.



**Figure 3.** Energy level diagram for the fluoride anion in sodium fluoride (chosen to avoid complications due to splitting of  $2p^{-2}$  in potassium fluoride). The origin of experimental data is shown on the diagram. Note the good correlation between the  $F^{-} K\alpha_{1,2}$  energy and the difference between the XPS  $1s$  and  $2p$  energies. The Auger energy can be compared with that of Albridge *et al.*<sup>6</sup> (654.6).

orbitals so that near parity of orbital contribution from potassium and fluorine might be expected in both bonding and anti-bonding orbitals. Since both of these orbitals will be active in the Auger process a trio of configurations is possible. Thomas and Weightman<sup>5</sup> suggest that if the difference Coulomb repulsion between localised hole pairs and delocalised hole pairs ( $\Delta U$ ) is taken into account then it is possible to estimate the relative intensities of Auger peaks resulting from these configurations. If  $\Delta E$  (energy difference between single hole molecular orbital states) and  $\Delta U$  are comparable, and for KF they might well be, then calculations suggest that two strong peaks and, to higher energy, one weak peak should result. Figure 2 shows two strong peaks in accord with this

model. The delocalisation of charge that could take place in the molecular orbitals will not of course affect the total electron density in the vicinity of the fluorine so that the Auger intensity should be the same for potassium fluoride as for other comparable ionic fluorides.

The possibility of delocalisation is however of vital importance for vacancies, which can lead to high-energy *X*-ray satellites only if they remain on the fluoride. The initial state for this process is  $1s^{-1}2p^{-1}$  and as can be seen from Figure 3 the 2p ionisation energy (*i.e.*  $1s^12p^6 \rightarrow 1s^12p^5$ ) is only slightly greater in the presence of a 1s hole than a 2p hole. Thus vacancy migration from fluoride to potassium would be quite possible and relaxation on fluorine, when it occurred, would then lead to normal  $K\alpha$  *X*-ray emission. If fluorine-potassium molecular orbitals are formed then the  $1s^{-1}2p^{-1}$  and  $2p^{-2}$  states derived from fluoride will both be split giving new states based on two and three configurations respectively. Thus not only will the intensity of the satellites be reduced because of the finite probability that the spectator hole will no longer be on fluorine but those satellite lines that are observed should be found over an increased energy range.

Although the arguments given above are presented in terms of a molecular orbital model exactly similar conclusions can be reached using the valence bond approach since the ionic structures (i)  $K^+(3p^6)F^+(2p^4)$  and (ii)  $K^{2+}(3p^5)F^0(2p^5)$  have similar energies [ignoring electrostatic effects (ii) is more stable than (i) by *ca.* 4 eV] and will therefore exhibit strong resonance. The postulate of temporary covalence between potassium  $K^+$  ( $3p^6$ ) and fluorine  $F^0$  ( $2p^5$ ) which enables a second vacancy to be delocalised thus allows the quite different

observations for potassium fluoride of peak splittings in Auger spectroscopy and satellite attenuation in *X*-ray spectroscopy to be understood.

Since the 4p ionisation energy for strontium is only 2.1 eV greater than that for the 3p orbital of potassium it seems probable that similar 'temporary covalence' could explain the extremely low relative intensity of the  $K\alpha_{3,4}$  peaks in strontium fluoride.

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