The Carbon–Fluorine Bond. A Study of the Role of Fluorine 2*p*-Orbitals using *X*-Ray Emission Spectroscopy

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Summary The extent to which fluorine 2*p* orbitals participate in covalent bond formation with carbon is estimated using *X*-ray emission spectroscopy.

The K_α *X*-ray emission of fluorine arises from the electronic transition $2p \rightarrow 1s$. All orbitals, atomic or molecular, will contribute to the intensity of the observed peak, depending upon the amount of fluorine 2*p* character present in them.[1] Here, the fluorine K_α peaks from sodium fluoride and from a tri-fluoromethyl group are compared. [The CF_3 group was present in the complex tris(hexafluoroacetylacetonato)-aluminium]. The spectra which are shown in Figure 1 were obtained from samples which had been pressed into a disc with terephthalic acid and irradiated with *X*-rays from a chromium anode 2·7 kW *X*-ray tube in a Philips PW 1410 spectrometer. The fluorescent *X*-rays from the sample were analysed using a rubidium acid phthalate crystal ($2d = 2612$ pm) with fine collimation and detected with a proportional counter (1 μm, window) and Harwell 2000 series electronics. Counts were taken for 5 min periods at pre-set angular positions. Each spectrum was scanned automatically and readings taken every 0·04° (2θ) in the range 88—93° (2θ).

Comparison of the two spectra shows that there is considerable low-energy structure present when fluorine is covalently bound to carbon which is not seen in the ionic sodium fluoride. The single main peak from sodium fluoride may be correlated with transitions from the three degenerate 2*p* orbitals of the fluorine anion. Similarly, peak D in the CF_3 spectrum corresponds to the two lone-pair orbitals present on each fluorine atom. However, the fluorine atoms are considerably closer in each CF_3 group than are fluorine anions in sodium fluoride. Stronger lone pair–lone pair repulsions are therefore to be expected in CF_3 than in NaF. Helium-(I) photoelectron spectra of compounds containing CF_3 groups show a characteristic set of peaks in the range 14·5—17·5 eV.[2] This correlates well with the K_α peak width at half height which is greater for trifluoromethyl (4·5 eV) than for sodium fluoride (3 eV).

The other peaks (A—C) that are observed in the CF_3

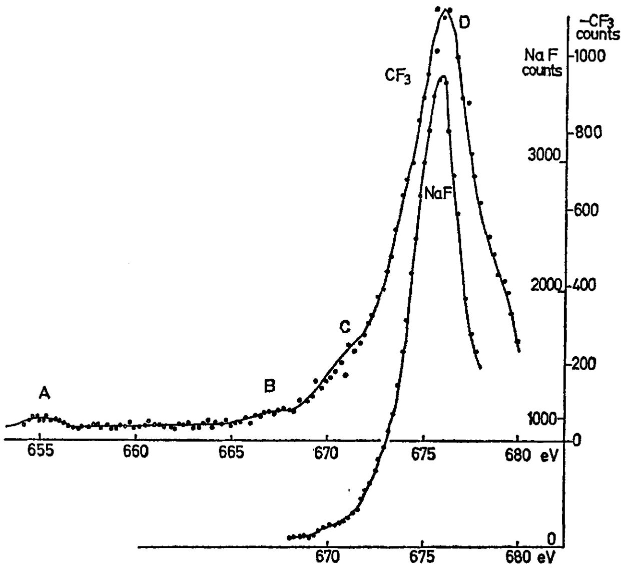

FIGURE 1. Fluorine $K\alpha$ emission spectra from a CF_3 group (upper curve, right hand vertical scale) and from sodium fluoride (lower curve, left hand vertical scale).

spectrum are presumably to be correlated with fluorine $2p$ character in various C–F molecular orbitals. A qualitative M.O. energy level diagram is shown in Figure 2, drawn assuming local C_{3v} symmetry. The direct relationship between the M.O.s and peaks A—C is readily seen. The three fluorine $2s$ orbitals and three fluorine $2p$ orbitals (one from each fluorine orientated along a C–F bond) will both give rise to symmetry orbitals of irreducible representations a_1 and e. Some mixing of fluorine $2s$ and $2p$ character is therefore possible. The extent to which $2p$ character enters M.O.s which are almost wholly F($2s$) in character is measured by the intensity of peak A. The a_1 carbon orbital will have both C($2s$) and C ($2p$) components and will therefore be more tightly bound than the carbon e orbitals which will be exclusively $2p$. B is thus to be associated with the $2a_1$ M.O. and C with the $2e$ orbital. It is hoped that more detailed work will permit the relative intensities of A, B, C, and D to be determined, but rough estimates based on peak heights are B:C:D = 6:20:110. If it is assumed that these intensities are directly related to the numbers of fluorine $2p$ electrons in the orbitals then D may be used as a reference, 12 electrons. The fluorine contribution to the $2e$ orbitals is thus *ca.* 55% and to the $2a_1$ orbital *ca.* 35%.

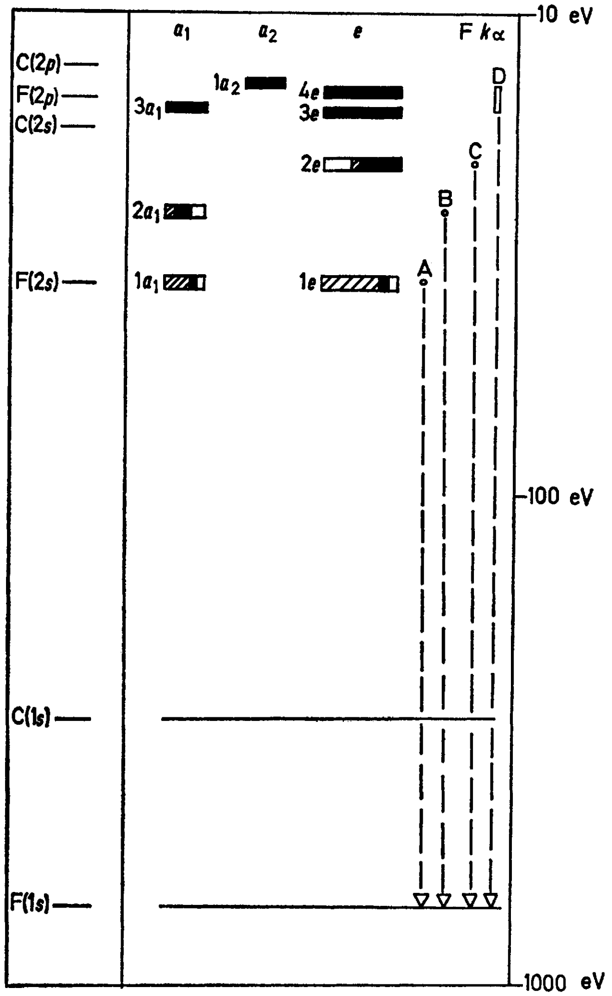

FIGURE 2. Qualitative M.O. energy level diagram. A.O.s are indicated on the left, M.O.s on the right. Fluorine $2p$ character: solid black, fluorine $2s$: diagonal hatching, carbon $2s$ and $2p$ (undifferentiated): blank. The proposed correlation between the peaks of Figure 1 and various M.O.s is shown on the far right.

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