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The X-Ray Photoelectron Spectra of Inorganic Molecules. XI[1]. Fluorine 1*s* Binding Energies in Metal Fluorides

Fluorine 1*s* binding energy measurements have been recorded for a variety of crystalline metal fluorides. Systems which have been studied are those containing either different or equivalent terminal *M*–F bonds, bridging *M*–F bonds or a mixture of both. Contrary to earlier literature reports, it is found in the present investigation that differences between fluorine 1*s* binding energies associated with these different bonds are very small (less than 0.5 eV), thereby suggesting that *XPS* measurements on metal fluorides are unlikely to be of routine use in distinguishing different fluorine environments.

Although several studies have been reported which deal with the fluorine 1*s* binding energies of crystalline inorganic compounds (*2–4*), little information is available on whether different fluorine environments can be distinguished in such phases. In these reports (*2–4*), few details were given of either fluorine 1*s* peak widths or peak shapes, knowledge of which is essential for extracting useful structural information. In view of our earlier findings (*5–7*) that differences in chlorine 2*p* binding energies between chloride ion and chlorine atoms in bridging and terminal metal–chlorine bonds can often be used to identify these structural units, we became interested in the possibility that different fluorine environments could also be differentiated by *XPS* measurements. This possibility certainly seemed reasonable in view of the recent results of fluorine 1*s* binding energy measurements on the *gaseous* fluorides PF_5, SF_4, and ClF_3 (*8*), in which the fluorine atoms in axial bonds were observed to have significantly higher binding energies than those in equatorial bonds.

The fluorine 1*s* binding energies of a variety of metal fluorides were recorded by us on a Hewlett–Packard 5950A ECSA spectrometer. Full details of the experimental procedure we used are described elsewhere (*6*, *9*). The data we obtained are presented in Table I, wherein the measured binding energies and FWHM values are reported together with the sources of the compounds which were studied.

The wide range of measured fluorine 1*s* binding energies is largely attributable to surface charging effects. However, since these peaks are both relatively narrow (FWHM values 1.4–2.1 eV) and symmetric in shape it is clear that the surface charging is fairly uniform. Since we are not particularly concerned in this study with absolute binding energies, *uniform* charging of the sample surface will not affect structural conclusions. Since the majority of complex fluoro-anions listed in Table I were studied as their potassium salts, it is useful to internally reference the fluorine 1*s* energies to some standard value of the potassium $2p_{3/2}$ energy, say 293.0 eV. When this is done, the fluorine 1*s* energies of these fluoro-anions fall in the much narrower range of 686.0 to 684.7 eV, consistent with the suggestion that charging is mainly responsible for this wide spread of fluorine 1*s* energies.

The complexes we have studied belong to the following structural types.

(a) Compounds 1, 7, 9, 10, 11, 15, and 16 containing equivalent terminal *M*–F bonds (*16*).

(b) Compounds 4, 5, and 6 containing two types of terminal *M*–F bonds, those which

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TABLE I

FLUORINE 1*s* BINDING ENERGIES OF METAL FLUORIDES

	Compound	Preparation	F 1*s*[c]	Other binding energies[c]
1	Na_2TiF_6	[a]	684.9(1.7)	—
2	ZrF_4	[a]	685.2(1.6)	—
3	K_2ZrF_6	Ref. (*10*)	684.0(1.7)	K $2p_{3/2}$, 291.9(1.4)
4	$K_2VOF_5 \cdot H_2O$	Ref. (*11*)	684.6(1.6)	K $2p_{3/2}$, 292.8(1.5)
5	$K_2MoO_2F_4 \cdot H_2O$	Ref. (*12*)	684.2(1.9)	K $2p_{3/2}$, 292.5(1.5)
6	$K_2WO_2F_4 \cdot H_2O$	Ref. (*12*)	685.3(2.1)	K $2p_{3/2}$, 293.1(1.3)
7	K_2MnF_6	Ref. (*13*)	683.9(1.5)	K $2p_{3/2}$, 292.0(1.4)
8	SnF_4	[a]	684.0(2.0)	Sn $3d_{5/2}$, 488.0(1.8)
9	K_2SnF_6	[b]	685.6(1.5)	K $2p_{3/2}$, 293.3(1.4) Sn $3d_{5/2}$, 487.9(1.3)
10	$K_2[(CH_3)_2SnF_4]$	[b]	685.4(1.4)	K $2p_{3/2}$, 293.3(1.3) Sn $3d_{5/2}$, 487.6(1.2)
11	$Cs_2[(CH_3)_2SnF_4]$	[b]	684.4(1.7)	Sn $3d_{5/2}$, 486.6(1.7)
12	$NaSbF_4$	Ref. (*14*)	684.1(1.9)	Sb $3d_{5/2}$, 530.4(1.5)
13	$NaSb_2F_7$	Ref. (*14*)	684.3(1.8)	Sb $3d_{5/2}$, 530.6(1.5)
14	$[Co(NH_3)_6]Sb_2F_9$	Ref. (*15*)	684.2(1.7)	Sb $3d_{5/2}$, 530.9(1.3) N 1*s*, 399.8(1.2)
15	K_2SiF_6	[a]	685.1(1.5)	K $2p_{3/2}$, 292.4(1.4)
16	KPF_6	[a]	687.6(1.6)	K $2p_{3/2}$, 294.6(1.6)

[a] Obtained from commercial source.

[b] Sample kindly provided by Professor R. S. Tobias.

[c] FWHM values are given in parentheses.

are either *trans*- to *M*=O or *M*–F bonds (*17*).

(c) Compound 2 containing only bridging *M*–F bonds (*18*).

(d) Compounds 3, 8, 12, 13, and 14 containing both bridging and terminal *M*–F bonds (*19–23*).

Although the broadest of the fluorine 1*s* peaks are invariably associated with compounds which possess two different fluorine environments, it is apparent from the data in Table I that the binding energy differences associated with these fluorine environments are sufficiently small to preclude their separation within the present limits of our instrumental resolution. These results are in contrast with the claim of Nefedov et al. (*3*) that for the zirconium(IV) fluoride complex K_2ZrF_6 "the overall profile of the F 1*s* line breaks down into two components with intensity ratio 2:1, the distance between them amounting to approximately 0.6 eV". These workers similarly report (*3*) that the fluorine 1*s* spectra of the *cis*-$[MO_2F_4]^{2-}$ anions [M = Mo or W] show a difference in the fluorine 1*s* energies of the fluorine atoms in the *trans* and *cis*-positions of 0.9–1.0 eV. No such differences were found by us in the spectra of these oxyfluoro-anions (Table I). The most obvious explanation for the differences between our results and those of Nefedov *et al.* (*3*) is that the spectra obtained by the latter workers are complicated by the occurrence of *differential* surface charging thereby leading to asymmetric broadening of the fluorine 1*s* peaks.

In contrast with the large differences we have previously found (*5–7*) between the chlorine 2*p* binding energies of many metal chlorides containing terminal and bridging *M*–Cl bonds, such differences which exist for *crystalline* metal fluorides are of a much smaller magnitude. Provided that relaxation effects are not particularly dominant, it is apparent that with the more ionic metal fluorides the variations in charge at the different fluorine atoms are significantly less than is the case with chlorine in transition metal chloride phases. Such a trend is in keeping with the polarizability difference $Cl^- > F^-$.

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