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PHOTO-ELECTRON SPECTRA OF FLUORIDES AND THE INFLUENCE OF THE MADELUNG POTENTIAL ON INNER SHELLS

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SUMMARY

The ionization energy *I* of the fluoride 1s shell is shown to vary from 695.7 to 687.8 eV in 40 solid compounds and has been compared with the value for four gaseous fluorides from the literature. The influence of the Madelung potential on potassium compounds and the combined influence of changing the oxidation state and the Madelung potential on iodine compounds have been studied from a comparative viewpoint. Central atoms with high oxidation numbers and small radii produce the highest *I* values in fluorides. The far-UV spectra and polarization effects in solid halides have also been discussed.

INTRODUCTION

In the last few years, it has become possible to measure ionization energies *I* both of penultimate delocalized molecular orbitals and of inner shells by photo-electron spectrometry. The two main techniques used involve irradiation of gaseous samples[1] with monochromatic photons of 21.2 or 40.8 eV energy or solid samples[2,3] with photons of 1253.6 or 1486.6 eV energy. We have started comparative work[4,5] on inorganic solids containing essentially all non-radioactive elements.

Fluorine is characterized[6] by existing in only one oxidation state (−1) in its compounds, and a study of the free element is difficult because of its high reactivity and (for our purpose) its very low boiling point. Hence, because of the invariant oxidation state of fluorine in its compounds, the chemical shift d*I* of ionization energies from one compound to another does not in this case depend on a variation in the oxidation state but on two other factors[7], *viz.*, the fractional[8] atomic charge δ, and the Madelung potential produced by the surrounding atoms. It can, in fact, be argued[9] that d*I* for inner shells is an indicator of changes of the Hartree potential $U(x,y,z)$ including the Madelung potential. Whereas the central field $U(r)$ in the atomic core is changed to the same extent over a fairly large region around the nucleus, and is in a way proportional to δ, this change is counteracted to a considerable extent by the Madelung potential, which may decrease the value of I by 10 to 20 eV in cations [4].

With the exception of the 4f shell in rare earths and the heavier elements [4,5], low values of I (below 50 eV) of greatest interest to the chemists are those producing weak signals with soft X-rays (say 1486.6 eV) will have only a small probability of ejecting an electron with almost as high a kinetic energy as the photon energy. In contrast, the 1s orbital of fluorine having a higher I value produced a very strong signal on our Varian IEE-15 instrument. The Uppsala group [10], who have studied gaseous CF_4 and SF_6 using soft X-rays, have found a most interesting electronic structure with energy I between 39 and 44 eV. This was caused by the interaction between the 2s orbitals of fluorine and in a particular homonuclear case [7] had an order of magnitude of I-times the overlap integral. This quantity can be shown [5] to be negligible for genuine inner shells. It is also interesting to compare this I value with that for a series [11] of fluorine-substituted methanes from CH_3F to CF_4.

RESULTS

Fluorine 1s orbitals

The I values obtained in this study corrected relative to *vacuo* and using I(C1s) of one-sided Scotch tape as an internal standard of reference are listed in Table 1. Arguments [4] have been advanced suggesting that this latter value should lie between 289 and 291 eV, and in this study it is proposed to define I by the relationship $I = I^* + C_{st}$ where I^* is the ionization energy recorded by the apparatus and C_{st} is the difference between 290.0 eV and the lowest C1s signal recorded, the solid sample measured being distributed as a powder on five-sixths of a cylinder covered with Scotch tape (No. 600 P from the 3M Company). A variation of 7.9 eV is observed between the largest and smallest values measured which may be related by the series

$$\begin{aligned}&\mathrm{CF_2(polymer) > CF_4(gas) \sim MgF_2 \sim CsSbF_6 > LaF_3 > SF_6(gas) > CHF_3(gas) \sim}\\&\mathrm{K_2GeF_6 \sim CeF_3 > KBF_4 \sim KPF_6 > NaF > Na_3AlF_6 > ThF_4 > K_2SiF_6 \sim}\\&\mathrm{ZrF_4 > SrF_2 > BaF_2 > GaF_3,\ 3H_2O \sim YbF_3 > LiF \sim K_2BeF_4 \sim SmF_3 > CaF_2 \sim}\\&\mathrm{K_2NbF_7 > KNiF_3 \sim K_2HfF_6 > CH_3F(gas) > Zn(H_2O)_6SiF_6 \sim BeF_2 \sim K_2TiF_6 \sim}\\&\mathrm{CdF_2 \sim K_2TaF_7 > K_2UF_6 > (NH_4)_3GaF_6 \sim RbF > (NH_4)_2In(H_2O)F_5 >}\\&\mathrm{(NH_4)_3ScF_6 > NiF_2,\ \ 4H_2O > KF > PbF_2 > (NH_4)_3CrF_6 \sim (NH_4)_2Fe(H_2O)F_5}\\&\mathrm{\gg CsF}\end{aligned} \tag{1}$$

which is in qualitative agreement with the concept of fractional atomic charges [6] and the Madelung potential V. It is possible [4] to correct for the influence of V if completely electrovalent bonding is assumed, i.e.,

$$\begin{array}{lllll} \text{LiF} & 692.8 - 12.5 = 680.3 & \text{CaF}_2 & 692.7 - 15.35 = 677.35 \\ \text{NaF} & 693.8 - 10.85 = 682.95 & \text{SrF}_2 & 693.45 - 14.3 = 679.15 \\ \text{KF} & 690.35 - 9.42 = 680.9 & \text{CdF}_2 & 692.05 - 15.5 = 676.55 \\ \text{RbF} & 691.3 - 8.9 = 682.4 & \text{BaF}_2 & 693.2 - 13.5 = 679.7 \\ \text{CsF} & 687.8 - 8.35 = 679.45 & & \end{array} \tag{2}$$

From this series it would appear that the gaseous ion F^- would have a value of I about 680 eV, some 14 to 15 eV below the values found in BF_4^-, CF_4, PF_6^- and SF_6. Although these four species are fairly covalent, they do not contain neutral fluorine for which the value of I could very well be close to 700 eV.

TABLE 1

IONIZATION ENERGIES I OF FLUORINE 1s RELATIVE TO VACUO USING THE SCOTCH TAPE CORRECTION C_{St} DEFINED IN THE TEXT (ALL VALUES IN eV)

	C_{St}	I(F1s)		C_{St}	I(F1s)
LiF	4.2	692.8	$Zn(H_2O)_6SiF_6$	4.85	692.15
BeF_2	5.3	692.1	$GaF_3.3H_2O$	5.0	692.9
K_2BeF_4	5.3	692.8	$(NH_4)_3GaF_6$	5.4	691.3
KBF_4	4.6	694.0	K_2GeF_6	4.7	694.1
CH_3F (Ref. 11)	—	692.4	RbF	4.4	691.3
CHF_3 (Ref. 11)	—	694.1	SrF_2	5.5	693.45
CF_4 (Ref. 11)	—	695.0	ZrF_4	4.4	693.5
CF_2 polymer	3.8	695.7	K_2NbF_7	5.0	692.7
NaF	5.1	693.8	CdF_2	4.75	692.05
MgF_2	5.1	695.0	$(NH_4)_2In(H_2O)F_5$	5.0	691.0
Na_3AlF_6	4.8	693.7	$CsSbF_6$	5.1	695.0
K_2SiF_6	4.8	693.5	CsF	4.1	687.8
KPF_6	4.5	694.0	BaF_2	4.7	693.2
SF_6 (Ref. 10)	—	694.6	LaF_3	4.7	694.8
KF	4.15	690.35	CeF_3	4.8	694.1
CaF_2	4.55	692.7	SmF_3	5.0	692.8
$(NH_4)_3ScF_6$	5.4	690.9	YbF_3	4.7	692.9
K_2TiF_6	4.45	692.1	K_2HfF_6	5.0	692.6
$(NH_4)_3CrF_6$	4.75	689.5	K_2TaF_7	4.5	692.0
$(NH_4)_2Fe(H_2O)F_5$	4.8	689.45	PbF_2	4.75	690.1
NiF_2, $4H_2O$	4.7	691.5	ThF_4	4.9	693.6
$KNiF_3$	4.5	692.6	K_2UF_6	4.9	691.9

The position of CsF at the end of the sequence depicted as (1) is even more surprising since caesium salts of many anions[4], like the iodides of many cations, usually exhibit abnormally high values of I. Although CsF is somewhat unpleasant to work with because of its hygroscopic nature, there is no serious reason to doubt the correctness of its position in the above sequence since the adsorbed water could be completely pumped off in a few minutes. The low value of I for $(NH_4)_3$-CrF_6 may be connected with the presence of three π-antibonding and no σ-antibonding electrons in the 3d-like orbitals of chromium(III). In addition, the Cr–F distances are unusually short, the electron density on the fluorine atoms being less affected by covalent bonding because of the delocalization of the three 3d-like orbitals. A similar low I value is also observed for $(NH_4)_2Fe(H_2O)F_5$.

Fluorine 2s orbitals

The variation of the signals corresponding to F2p in the fluorides listed in equation (2) has already been discussed[4] and found to be in good agreement with the Madelung potential if a value of $I=290.0$ eV is accepted as correct for the C1s electrons in Scotch tape. Signals corresponding to F2s electrons in 26 compounds have been measured in this study by exposing the compounds for 2000 s or more. The difference I(F1s) $-I$(F2s) was found to be 655.3 eV with an average deviation 0.6 eV, which is not much larger than the experimental uncertainty. In cubic crystals, such as LiF, the signal (which occurs in this case at 37.4 eV) was not split but only broadened by the formation of energy bands. In contrast much less detailed structures were found for F2s and F2p electrons in BF_4^-, SiF_6^{-2} and PF_6^- than those reported[10] for the isoelectronic neutral molecules CF_4 and SF_6.

TABLE 2

IONIZATION ENERGIES I OF POTASSIUM ORBITALS

	C_{st}	$I(K2p_{1/2})$	$I(K2p_{3/2})$	I(K3s)	I(K3p)
K_2BeF_4	5.3	303.8	301.3	—	—
K_2SiF_6	4.8	303.7	301.2	41.0	25.2
KPF_6	4.5	303.8	301.05	39.0	24.75
KBF_4	4.6	303.4	301.0	39.6	24.8
KI	4.7	303.75	301.0	40.7	24.8
$KNiF_3$	4.5	303.7	300.9	(38)	25.2
K_2HfF_6	5.0	303.5	300.8	(41)	—
K_2NbF_7	5.0	303.2	300.5	40	—
KIO_4	5.3	303.4	300.5	40.1	24.3
K_2TiF_6	4.45	303.1	300.45	(36.9)	24.3
KF	4.15	303.0	300.35	40.3	24.15
KCl	4.8	303.0	300.3	40.2	23.9
KIO_3	5.3	303.1	300.2	40.5	23.8
$KClO_4$	4.8	302.5	299.8	39.9	23.9
KBr	4.6	302.4	299.8	39.3	23.3
K_2TaF_7	4.5	302.3	299.6	(36)	23.8
$KReO_4$	3.7	302.1	299.4	—	23.6
$K_2Ru(NO)Cl_5$	4.8	302.1	299.4	39.4	23.2
K_2ReBr_6	4.8	302.1	299.3	39.4	22.9
K_2PdCl_4	4.8	301.9	299.3	39.2	23.2
KNO_3	5.1	301.4	298.8	38.9	22.7
K_2PtBr_6	2.6	301.45	298.8	39.4	23.1
K_2ReCl_6	3.7	301.3	298.7	39.0	22.4
$K_4Fe(CN)_6$	5.1	301.3	298.6	39.0	22.8
$K_3Cr(NCS)_6$	4.8	301.1	298.4	38.7	22.6
K_2OsCl_6	3.8	301.1	298.4	38.7	22.7
$K_2Pt(SCN)_6$	4.8	301.0	298.3	38.5	22.5
KSeCN	3.6	301.0	298.1	—	—
$K_3Fe(CN)_6$	5.4	300.5	297.9	38.1	21.9

However, although the signal to noise ratio is not particularly favourable in this study, it was possible to recognize shoulders at 20 and 18 kK on the 16 kK signal of KBF_4 whereas K_2SiF_6 shows a single F2p signal at 16 kK. The main F2s signals occur at 38.7 kK in both these compounds, but a weaker signal at a higher I value would be masked by the K3s signal.

Potassium

The fractional charge of potassium would not be expected to deviate significantly from $+1$ in its compounds. In Table 2 four different signals from 29 selected potassium salts have been arranged in order of decreasing I value for the $2p_3/_2$ electrons. The other component $2p_1/_2$, is weaker and not so well defined. The observed variation of 3.4 eV is presumably due in part to a weaker (electron-repelling) Madelung potential in the case of larger anions, and in particular of fluoride-containing anions. This however cannot be the whole explanation. Thus, the fact that the chloro complexes of the noble metals induce such low I values for potassium is completely unexpected. When V is added, the corrected I value for $2p_3/_2$ for K^+ would be 309.8 eV for KF, 308.2 eV for KCl, 307.45 eV for KBr and 308.1 eV for KI. These minor deviations from the Madelung description are similar to those observed [4] for K3p.

In contrast, the K3s signals listed in Table 2 vary in a much more unpredictable fashion. In addition to the possible larger experimental uncertainty in this case, these signals might correspond to examples of non-diagonal elements of the heteronuclear type [7] with orbitals of adjacent atoms having comparable I values.

Iodine

Some of the oldest established cases[12] of chemical shifts in photo-electron spectra are those of iodine(VII) and iodine(V) which have I values 6 and 5 eV respectively higher than comparable iodides. This apparently prominent influence of the oxidation state on the ionization energy does not always apply in this direction. Thus, Tl_2O_3 has lower a I value than a large number of thallium(I) compounds and PbO_2 a lower I value than all known lead(II) compounds [4, 5]. It is obvious that here both the Madelung potential and the general chemical environment play a role. Thus, $I(Sb3d_3/_2)$ for $CsSbF_6$ is 551.95 eV in comparison with 548.7 eV for $CsSbCl_6$ and 547.1 eV for $KSb(OH)_6$. This observed variation with these ligands is far larger than the difference between Sb(V) and Sb(III) with the same ligands. $I(Sb3d_5/_2)$ occurs at 542.45 eV in $CsSbF_6$ whereas it almost coincides with the oxygen 1s signal in other antimony compounds.

By analogy to the variations listed in Table 2, it has been firmly established that large tetra-alkyl-ammonium ions produce a weaker Madelung potential than alkali metal ions; thus I(I5p) has been determined [4] as 11.0 eV in KI. Unfortunately, in our studies the signals produced in the valence region were too weak to allow a quantitative estimation of the decrease of ionization energy for $NR_4^+I^-$, although the lowest I value seems to be close to 8 eV for both R is CH_3 and C_2H_5. In contrast a clearly defined decrease of between 1.3 and 3.2 eV occurs with both the 3d and 4d ionization energies, as shown in Table 3. From the chemical view point, there is little doubt that the iodides of Cs^+ and the larger cations are particularly reducing, readily forming I_3^-, in the same way as Cs_2O is readily oxidized to the superoxide CsO_2 and BaO to the peroxide BaO_2. However, from the physical viewpoint the low dielectric constant of the iodides of organic cations must be taken into account. In these compounds the environment of the I^- ion is not unlike its situation in the gaseous state[13,14] where its ionization energy is 3.06 eV (in comparison with 3.40 eV for F^-).

TABLE 3

IONIZATION ENERGIES I OF IODINE ORBITALS

	C_{st}	I(I3d$_{3/2}$)	I(I3d$_{5/2}$)	I(I4d)
KIO_4	5.3	644.3	632.8	63.7
$NaIO_4$	4.75	643.75	632.25	63.35
Na_5IO_6	5.25	643.25	631.65	62.65
KIO_3	5.3	642.5	631.0	62.1
NaI	5.6	638.9	627.3	57.6
CsI	5.15	638.55	627.0	57.95
KI	4.7	638.5	626.9	57.4
CdI_2	4.7	638.4	626.8	58.3
K_2HgI_4	4.6	637.6	626.1	57.3
$CsBiI_4$	5.0	637.5	626.0	57.6
BiI_3	5.0	637.25	625.8	57.8
$N(C_2H_5)_4I$	4.5	636.9	625.6	54.1
K_2PtI_6	4.6	636.5	624.9	56.3
TlI	4.85	636.25	624.75	56.25
Cs_2OsI_6	5.7	635.7	624.15	56.0
$N(CH_3)_4I$	4.9	635.6	624.15	54.3
$N(C_4H_9)_4I$	4.7	635.1	623.6	54.6

Even 40 years ago, it was already recognized[15] that emission and absorption spectra in the soft X-ray region involving the chlorine 1s orbital apparently gave the surprising impression that chloride ligands coordinated to transition group central atoms behave as if they were even more negative than electrovalent chlorides. Similar results have been obtained for d-group octahedral hexachloro and quadratic tetrachloro complexes relative to KCl, where I(Cl2p) decreases to 203 or 204 eV in comparison with 205.45 eV for KCl and, somewhat unexpectedly, with 207.6 and 207.3 eV obtained in two independent measurements of CsCl. This variation may be compared with the value of I(S2p) for sodium thiosulphate where the central and terminal sulphur atoms in $S_2O_3^{2-}$ have I values of 173.8 eV and

167.8 eV respectively. From Table 3 it will be seen that iodides of heavy metals have I(3d) values between 0.8 to 2.7 eV lower than for KI and CsI while there is much less variation in the I(4d) values. A particularly interesting case is Cs_2OsI_6, which has I values among the lowest known[16]. Unfortunately, I(I4d) is virtually coincident with I(Os4f) but despite this difficulty it appears that inter-ligand interactions split the former signal to I values of 56.0 and 54.8 eV. K_2PtI_6 does not suffer from such interference and exhibits I(Pt4f) at 81.2 and 78.4 eV and possesses a structure for I4d with a baricenter at 56.3 eV but with shoulders at 56.6 and 56 eV. I(Pt5d) produces a broad signal at the expected position[4] at 9.6 eV.

It is also interesting to compare the photo-electron spectra with the corresponding absorption spectra in the region from 10 to 200 eV. Thus, KI shows a structure[17] due to iodide 4d excitation at 54 eV followed by a broad maximum at 94 eV. Similar behaviour exhibited by gaseous and solidified xenon[18] is due to the unusual dependence of the ionization probability on the photon energy for high l-values, as has also been discussed [4] in connection with the strong 4f signals in the photo-electron spectrum of metallic gold. KBr also exhibits absorption bands[17] due to bromide 3d excitation which start at 74 eV. It may seem surprising that these values (which are not perturbed by Fermi levels in non-metallic compounds) are lower than the I values of 75.7 eV for KBr and 57.4 eV for KI as observed using photo-electron spectra. We believe that the absorption bands at lowest energy value correspond to excited states having one electron in a fairly extended p-like orbital, and that the charge separation effect[19,20] is sufficient to stabilize this state relative to the ionized system formed by loss of an electron to the surrounding vacuum. Even if the average radius of the p-like orbital is as large as 6 Å, the charge separation effect still stabilizes the excited state to the extent of 2.4 eV. This problem is also related to the suggestion[2] that the electron affinity of the lowest vacant orbitals of alkali metal halide crystals is very low, and that photo-electron spectra can be standardized by assuming that the first absorption band in the far ultra-violet has approximately the same photon energy as that needed to ionize the most weakly bonded p shell of the halide. This suggestion produces I values some 3 eV lower than those reported here[4].

CONCLUSIONS

The variation of 7.9 eV observed in the ionization energy of the fluorine 1s orbital in the compounds studied is perhaps not surprising in comparison with the range of 4.3 eV in the I(Fe3p) values found[21] in iron(III) complexes or the range of 5.7 eV for $I(Ni2p_{3/2})$ in nickel(II) complexes [4]. From the results listed for the potassium salts in Table 2 and from those for the electrovalent iodides listed in Table 3 it may be seen that varying the Madelung potential alone generally produces a variation in I of only approximately 3 eV. It is, however, difficult to estimate the experimental error associated with measurements on a particular compound for, as is frequently found in the natural sciences, the distribution of the results does not apparently follow a simple Gaussian error curve, and it would be meaningless to attempt a treatment involving least squares. On repetition, measurements usually varied within ± 0.5 eV of the original value.

As for visible and UV spectra[22,23] the problems associated with the interpretation of results of photo-electron spectrometry may be discussed under two headings: the understanding of the distribution of energy levels (such as the penultimate molecular orbital most readily studied in gaseous molecules[1]) and the correlation of the spectra with chemical properties. In this case, the higher oxidation number of the central atom and the smaller ionic radius (*cf.* B(III) and Sm(III)) produce a higher I value for fluoride ligands. There is little doubt that CsF and $NR_4^+F^-$ (provided that they can be prepared without an associated strongly hydrogen-bonded set of water molecules) contain fluoride which is far more reducing than that in most conventional fluorides. It is also striking that equation (1) above is virtually the order of anti-base (Lewis acid) character in the listed compounds, $CsSbF_6$ and CsF having extreme properties in this sense.

The known standard oxidation potentials E_0 extended over a range of 3 V on either side of the hydrogen potential. It is quite clear that the I values of the loosest bound molecular orbitals are some 3 eV higher than the chemical ionization energy (E_0+4.5 eV), the latter quantity having been connected with hydration energy differences[6,24]. This major difference can only be explained by assuming that because of their adiabatic character electrochemical reactions have sufficient time to rearrange the internuclear distances to their new equilibrium values, whereas the I values reported here refer to "vertical" transitions which preserve the internuclear distances.

It may seem paradoxical that although the electrostatic model of the ligand field theory has been abandoned since 1956 as a reasonable description of the energy levels of transition group complexes[22,25] that, at the same time, the Madelung potential $V(x,y,z)$ is considered to be important for the description of the chemical shift of I values. This apparent contradiction may be understood when it is realized that the spherically-symmetrical component $V(r)$ of the Madelung potential makes a major contribution to the variation of the Hartree potential from one compound of the same element to another, whereas the electrostatic model of the ligand field only considers the much smaller deviation $V-V(r)$ from the spherically-symmetrical Madelung potential. In contrast, the energy differences between the five d-like or the seven *f* orbitals in the above compounds are connected with the kinetic energy operator in the bond region[7] as are also the interactions between fluorine 2s orbitals of adjacent ligands as studied by photo-electron spectrometry[5,10].

Deviations from a straightforward Madelung potential may influence the I values in two ways. On the one hand, highly polarizable neighbour atoms may stabilize the ground state to such an extent that the ionization is made more difficult to the extent of some 2 eV. This may explain the unexpectedly high *I* values for caesium salts[4] (with the exception of CsF) and for most iodides, and would also partly explain the discrepancy between far-UV absorption spectra[17] and *I* values for solid bromides and iodides. On the other hand, the results in Table 2 for potassium salts exhibit an almost perfect arrangement in terms of Pearson's classification of the anion as a hard or soft base (again with the exception of iodide). From careful quantum mechanical studies of the ten-electron systems methane and neon[26], it is known that the main peak in the photo-electron spectrum has an energy 15 or 20 eV, respectively, below the value calculated for the eight "frozen" outer electrons, but agrees within 1 eV with the difference from the Hartree–Fock solution with adapted (contracted) orbitals for the ionized system. Hence, it is conceivable that neighbour anions with mobile electron density (such as complexes of heavy halides and pseudo-halides) decrease the *I* value by means of this rapid contraction to a much greater extent than is true for fluorine containing anions. In other words, the static polarization of the ground state increases *I* and the dynamic deviation from the behaviour described by Koopmans[2] decreases *I* by several eV. This effect is of general importance in the interpretation of X-ray-induced photo-electron spectra of inorganic solids. However, in transition group and post-transition group compounds, a major contribution to the chemical shift d*I* is the variation of the fractional charge[6, 8], and for a given element, the fluoride ion usually takes an extreme position with exceptionally high *I* values for the inner shells.

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