MEASUREMENTS OF PHOTO-ELECTRON SPECTRA AND CHARGING EFFECTS IN FLUORIDES, IODATES AND OXIDES

CHRISTIAN K. JØRGENSEN AND HERVÉ BERTHOU

Département de Chimie physique, Université de Genève, 1211 Geneva 4 (Switzerland)

(Received August 15, 1972)

SUMMARY

The ionization energies of inner electron shells have been measured without (I) and including (I') a correction for the charging effect of non-conducting solid samples (derived from the two different Scotch tape C1s signals observed) for the fluorides, iodates and oxides of 25 elements with a definite oxidation state z. Whereas the difference between the I' values for the fluoride and the oxide is close to z eV in most cases, this difference almost vanishes in Hg^{II} and is small in several other post-transition group elements.

INTRODUCTION

We have recently discussed[1] the photo-electron spectra of 40 solid fluorides measured on a Varian IEE-15 spectrometer using 1486.6 eV photons originating at an aluminium anti-cathode. It is normally suggested that the observed signals, which possess relatively sharp maxima (of half-width ∼1 eV) and correspond to the probability distribution of the kinetic energy of the ejected electrons, are related to the ionization energy I^* of the inner electron shells relative to the Fermi level of the apparatus by the simple formula

$$I^* = 1482.0 \text{ eV} - E_{kin} \tag{1}$$

where the work function of metallic copper (4.6 eV) has been subtracted from the photon energy. With non-conducting samples it is useful to use the strong signals of an internal reference compound for comparative purposes, and it has been suggested[2] that values of the ionization energies I relative to *vacuo* could be obtained by adding a correction constant C_{st} to the I^* values measured as above. The constant C_{st} is the difference between 290 eV and the C1s signal of Scotch tape and usually has a value between 4 and 5.5 eV. It has been argued that the adhesive material used on one-sided Scotch tape (No. 600 P from the 3M Company)

is an aliphatic hydrocarbon (polymerized isoprene) which would be expected to have a value of I (C1s) close to 290 eV in a similar manner to all other materials having a composition close to CH_2. This suggestion is, in fact, supported by the good agreement observed between the explanation for the Madelung potential of almost ionic crystals and the I values of the most weakly bound p shell of cations and anions obtained using this method.

However, measurements involving finely divided metals[3,4], such as Au, and oxides, such as Tl_2O_3, mixed with insulating powders, such as MgF_2 and $BaSO_4$, have shown that the I values obtained for the metals are 2–3 eV higher when they are insulated than when they are connected electrically to the apparatus, and that the presence of gold powder has only a marginal influence on the I values of non-conducting compounds. The most plausible explanation of this observation is that the sample possesses a quasi-stationary positive potential V which is virtually independent of the intensity and of the extent of X-ray irradiation. It has been suggested[5] that V has a definite value determined by the difference between the lower limit of the empty conduction band of the sample and the Fermi level of the metallic support, which explains why a moderate current is maintained in the quasi-stationary state. This explanation apparently precludes the possibility of measuring chemical shifts, dI, of solid samples since the region where I values may be measured has a width equal to 8 eV for fluorides[1], and for nearly all elements[5] is between 2 and 6 eV for compounds in the same oxidation state: overlap occurs to a considerable extent, and inversions have been found, e.g. Co^{III}, Tl_2O_3 and PbO_2 have lower I values than cobalt(II), thallium(I) and lead(II) compounds.

A way out of this dilemma has been suggested by Bremser and Linnemann[6]. Many salts have C1s regions which exhibit additional signals or shoulders at somewhat higher I^* values than that of pure Scotch tape. During the last two years, it has been suggested that such additional signals 4 eV distant from that due to pure Scotch tape are due to carbonate on the sample surface and those 2 eV distant are due to traces of various alcohols (cellulose from filter paper, solvents used in the preparation or from oxidation of the hydrocarbon) but, although such impurities must occur in some cases, there is little doubt that the signals of comparable intensity at an I^* value 3.8 eV higher in NaF, 2.2 eV in NaCl, 2.4 eV in NaBr and 2.8 eV in NaI must be due to some other cause. An alternative explanation[6] is that the distance between the two C1s signals is simply equal to V. This quantity is particularly large for certain anhydrous fluorides, e.g. for MgF_2 it has a value of 4.3 eV, for LaF_3 4.7 eV and for LuF_3 5.2 eV (the largest known value), probably indicating that these crystals lack a positive electron affinity. On the other hand, V is difficult to measure when it is less than 2 eV, and there is some evidence that it is very small for conjugated systems such as tetraphenylborates and tetraphenyl-arsonium and methylene blue salts. Since the value I for a given element is normally particularly high for the fluoride (and lowest for the sulphides and for complexes

with sulphur-containing ligands), it is not unreasonable to suggest that the values mentioned above merely reflect the high V values observed for many fluorides (but not for RbF and CsF). It is possible to define the ionization energy corrected for charging effects by the relationship:

$$I' = I - V = I^* + C'_{st} \tag{2}$$

where C'_{st} refers to the higher of the two I^* values observed for C1s. In practice, the typical range[5] of chemical shifts dI' is about two-thirds of the range dI and for this reason the correction for the charging effects only accounts for about a third of the total I variation. In addition, it is even possible to measure I' values with an average precision of ± 0.2 eV whereas I values may be reproduced to $\sim \pm 0.5$ eV on the average. It should also be noted that the largest V values greater than 4 eV tend to be accompanied by high C_{st} values of between 5 and 6 eV, an effect which also occurs with metallic powders which exhibit vanishing values of V. This effect may be connected with the trapping of a small number of electrons on the Scotch tape (which probably exhibits a weak electron affinity) giving rise to a negative potential under these particular conditions.

RESULTS AND DISCUSSION

Table 1 gives the I and I' values for fluorides, iodates (which frequently can be precipitated in an anhydrous state from aqueous solution[5]) and oxides of 25 elements exhibiting definite oxidation states. One or several nlj values giving the strongest signals[7] are also included. For comparison, the lowest I values observed in our study of 600 compounds[5] are also given; in a number of cases these refer to the oxide. It is, presumably, fortuitous that for Mg^{II} and Ca^{II} these low I values coincide with the lowest I' values. The values given in parenthesis refer to the fluoro complexes $(NH_4)_2[In(H_2O)F_5]$ and K_2HfF_6. Nickel(II) fluoride and calcium(II), nickel(II) and copper(II) iodates presumably contain water of crystallization[5].

For most elements having an oxidation state z, the difference between the I' value for the fluoride and for the oxide (given in the last column) is close to z eV. This is also true for gaseous CF_4 and CO_2. The difference tends to decrease in the heavier lanthanides and Hf^{IV}; the very small difference (which is close to zero) for Hg^{II} is, however, most interesting. It might be argued that CdF_2 (which also shows an unexpectedly low value of I') and HgF_2 are unusual in that they exist as eight-coordinated fluorides with exceptionally long internuclear distances. Although this may contribute to the low I' values, we believe that this behaviour is more likely to be connected with a general trend in the immediate post-transition group elements. Table 1 shows that a similar, although not quite so pronounced, effect is observed for In^{III}, Tl^I, Pb^{II} and Bi^{III}. The values of $I(F1s) = 690.0$ eV and $I'(F1s) = 688.0$ eV for HgF_2 are also unusually low being slightly below the values for PbF_2.

TABLE 1

IONIZATION ENERGIES OF INNER SHELLS (in eV) WITHOUT (I) AND WITH (I') CORRECTION FOR THE CHARGING EFFECTS V DESCRIBED IN THE TEXT

		Fluoride		Iodate		Oxide		Lowest known I	Difference between I' values of fluoride and oxide
		I	I'	I	I'	I	I'		
Be^{II}	Be1s	123.1	120.8	—	—	121.6	119.3	118.9	1.5
C^{V}	C1s	—	301.8	—	—	—	297.5	289	4.3
Mg^{II}	Mg1s	1314.1	1309.8	—	—	1311.3	1307.7	1307.7	2.1
Ca^{II}	Ca2p$_{3/2}$	356.1	352.9	354.7	352.3	—	—	352.3	—
Co^{II}	Co2p$_{3/2}$	792.1	787.8	787.9	785.8	—	—	786.9	—
Ni^{II}	Ni2p$_{3/2}$	864.4	862.3	863.9	861.5	862.4	860.1	858.7	2.2
Cu^{II}	Cu2p$_{3/2}$	943.3	941.1	941.7	939.6	941.5	938.8	937.3	2.3
Y^{III}	Y3p$_{1/2}$	311.5	307.8	309.6	307.0	306.9	—	306.9	3
	Y3d$_{5/2}$	168.5	164.8	166.3	163.7	163.6	—	163.6	3
Zr^{IV}	Zr3p$_{3/2}$	343.8	341.2	341.1	338.6	339.2	—	339.2	4
	Zr3d$_{5/2}$	193.2	190.6	190.5	188.0	188.3	—	188.3	4
Cd^{II}	Cd3d$_{5/2}$	412.4	410.6	—	—	412.8	410.2	410.7	0.4
In^{II}	In3d$_{5/2}$	(452.0)	(450.8)	453.3	450.5	449.6	—	449.6	—
Ba^{II}	Ba3d$_{5/2}$	789.3	785.0	787.2	784.5	—	—	—	—
La^{III}	La3d$_{5/2}$	847.0	842.3	843.9	840.6	840.9	838.9	840.9	3.4
Sm^{III}	Sm3d$_{5/2}$	1091.6	1088.6	1091.4	1088.5	1090.3	1087.7	1090.3	0.9
Eu^{III}	Eu3d$_{5/2}$	1143.8	1140.0	1143.0	1139.7	1141.3	1138.4	1141.3	1.6
Gd^{III}	Gd3d$_{5/2}$	1196.6	1193.0	1195.3	1192.1	1193.0	1191.0	1193.0	2.0
	Gd4d	152.5	148.9	151.6	148.4	149.3	147.3	149.3	1.6
Er^{III}	Er4d	178.8	175.3	177.1	174.8	177.0	173.9	177	1.4
Yb^{III}	Yb4d	194.7	192.2	193.9	191.2	189.2	—	189.2	3
	Yb4f	16.7	14.2	16.0	13.3	13.6	—	13.6	2
Lu^{II}	Lu4d$_{5/2}$	208.7	203.5	204.8	202.3	203.9	201.8	203.9	1.7
	Lu4f$_{7/2}$	20.5	15.3	16.8	14.3	16.0	13.9	16.0	1.4
Hf^{IV}	Hf4d$_{5/2}$	(222.4)	(220.1)	221.9	219.5	220.8	218.5	219.5	1.6
	Hf4f$_{7/2}$	(26.0)	(23.7)	25.6	23.2	25.0	22.7	23.2	1.0

Table 1 *(continued)*

Hg^II	Hg4d$_{5/2}$	366.8	364.8	366.6	364.5	367.0	364.7	364.9	0.1
	Hg4f$_{7/2}$	108.5	106.5	107.9	105.8	108.3	106.0	106.6	0.5
	Hg5d$_{5/2}$	16.3	14.3	16.2	14.1	16.3	14.0	—	0.3
Tl^I	Tl4f$_{7/2}$	127.2	124.6	126.9	124.3	—	—	124.4	—
	Tl5d$_{5/2}$	22.0	19.4	21.7	19.1	—	—	19.1	—
Pb^II	Pb4f$_{7/2}$	145.9	144.1	146.9	144.3	144.1	—	143.3	—
Bi^III	Bi4f$_{7/2}$	167.8	165.7	166.9	—	166.8	164.2	164.9	1.5
	Bi5d$_{5/2}$	34.7	32.6	33.9	—	33.8	31.2	31.9	1.4
Th^IV	Th4f$_{7/2}$	345.4	341.8	343.5	341.0	342.6	339.0	341.5	2.8
	Th5d$_{5/2}$	97.3	93.7	95.5	93.0	94.5	90.9	93.5	2.8

It is not possible to conclude unequivocally that the small differences between the I' values of the fluorides and the oxides are due to the 'soft' character of the cation according to the definitions proposed by Pearson (which may be connected with the properties of the continuum of one-electron functions having positive energy[8]). Nevertheless, it is still true that not only do the I values[1] of the potassium salts follow Pearson's series of anion 'softness' (with the clear-cut exception of the iodide), but also the I' values determined[5] for $K2p_{3/2}$ for 28 potassium salts behave in the same way, varying from 299.2 eV for KBF_4 and KPF_6 through values such as 298.5 eV for K_2BeF_4, K_2NbF_7 and K_2HfF_6 to 296.5 eV for KSeCN. It would indeed be surprising if the inner shell of the potassium ion could vary its ionization energy by 2.7 eV or 62 kcal mole^{-1}, and for this reason we believe[5] that this result may be explained in terms of the less extensive modification of the electron density of the ionized system in the case of fluoride-containing anions.

Whereas the chemical shifts dI' in Table 1 are smaller than in gaseous molecules containing elements (such as nitrogen and sulphur) which are capable of changing their oxidation states by eight units, they are still far too systematic (and an order of magnitude larger than their reproductibility) to be due to experimental errors. We believe that I' values are a more reliable measure of the actual ionization energy relative to *vacuo* than I values, but that these values may still be a little too small, as suggested by the accompanying variations in the values of C_{st}. If the physical origin of the difference between I and I' is indeed the quasi-stationary potential V as suggested above[5], it is not feasible to use this method to determine the absolute ionization energies of mixtures of non-conducting samples because the quasi-stationary charge distribution sometimes gives rise to different values of V for the same constituent. Fluorides of many bivalent, trivalent and quadrivalent metals exhibit rather extreme behaviour in this respect.

REFERENCES

1 C. K. JØRGENSEN, H. BERTHOU AND L. BALSENC, *J. Fluorine Chem.*, *1* (1972) 327.
2 C. K. JØRGENSEN, *Chimia (Switz.)*, 25 (1971) 213.
3 D. J. HNATOWICH, J. HUDIS, M. L. PERLMAN AND R. C. RAGAINI, *J. Appl. Phys.*, 42 (1971) 4883.
4 C. K. JØRGENSEN, *Structure and Bonding*, *13* (1973) 199.
5 C. K. JØRGENSEN AND H. BERTHOU, *Mat. Fys. Medd. Danske Vidensk. Selskab*, *38* (1972) No. 15.
6 W. BREMSER AND F. LINNEMANN, *Chem.-Ztg. (Heidelberg)*, 95 (1971) 1011.
7 C. K. JØRGENSEN AND H. BERTHOU, *Discuss. Faraday Soc.*, *54* (1972) in press.
8 C. K. JØRGENSEN, *Modern Aspects of Ligand Field Theory*, North-Holland Publ. Co., Amsterdam, 1971.