Multiplet Splitting of X-Ray Photoelectron Lines of Chromium Complexes. The Effect of Covalency on the 2p Core Level Spin–Orbit Separation

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The multiplet structure of the 2p photoelectron lines of a series of chromium compounds has been investigated and the contributions made to the $2p_{3/2}$–$2p_{1/2}$ doublet separation by spin–orbit coupling and exchange interaction has been assessed. The spin–orbit coupling constant, ξ_{2p}, has been shown to be essentially invariant over the oxidation state range 0 to VI, and it has thus been possible to describe the alterations in the 2p separations in terms of covalency effects which modify the degree of exchange interaction.

Introduction

Electrostatic and exchange interactions can operate to produce multiplet structure in the photoelectron spectra of open shell systems[1]. Such splittings result from coupling between core electrons and non-spherically symmetric electrostatic environments or unpaired electrons. Several cases of exchange splitting have been reported for transition metal complexes[2–11], but in most cases the emphasis has centred around splittings in the 3s spectra arising from exchange interactions between the partially filled 3s and 3d orbitals. These splittings are larger than those involving inner core electrons and thus more readily observed. For example, Fadley *et al.*[2] and Fadley and Shirley[3] have reported splittings of 6.5 eV between the 3s levels in MnF_2 as compared to theoretical splittings of 11.3 eV for the isolated Mn(II) ion and 6.8 eV for the MnF_6^{4-} ion[12], whereas Carver *et al.*[4] have reported splittings in the range 0.2 to 7.3 eV for various chromium, manganese, iron and cobalt complexes.

However, the situation regarding lines arising from photoionisation of levels for which the orbital angular momentum does not equal zero is considerably more complex. The coupling of both spin and orbital angular momentum of electrons in such orbitals gives rise to a number of possible LS combinations resulting in multiplet states. Thus, in this situation simple doublets are not observed, as in the 3s cases above, but rather, the peaks are broadened and shifted. As will be shown

below it is the degree to which the $2p_{3/2}$–$2p_{1/2}$ spin–orbit doublet components are altered that provides the key to assessing the relative contributions of exchange interaction and covalency. Indirect evidence for multiplet splitting of 2p lines from cobalt complexes has been obtained by Frost *et al.*[5], and more recently Briggs and Gibson have observed direct evidence[11] for multiplet splitting of cobalt 2p peaks in square planar Co(II) complexes. For the chromium systems investigated here the possible effect of covalency upon the spin–orbit coupling constant has also been considered. This could be an important consideration since the small perturbations ($\cong 1$ eV) in the $2p_{3/2}$–$2p_{1/2}$ separation ($\cong 15$ eV) which are explained by reference to the jj coupling scheme of Nefedov[13] (see below) could easily be overshadowed by small changes in the spin–orbit coupling constant for the 2p shell ξ_{2p}.

The ESCA studies of chromium systems which have appeared in the literature[4, 6, 14–19] have paid little attention to 2p multiplet effects and we report here the 2p data from a series of compounds in which chromium is present in a formal oxidation state of 0, II, III or VI. The results indicate that the 2p spin–orbit coupling constant, ξ_{2p}, remains essentially invariant over the oxidation state range and that screening effects at this level within the chromium atom are not affected by the changes in the d level population. It is possible therefore to attribute the changes in the $2p_{3/2}$–$2p_{1/2}$ separations for Cr(III) compounds to covalency effects.

Experimental

Binding energies were measured on a Vacuum Generators ESCA 2 X-ray photoelectron spectrometer using Al(K_α) X-radiation (1486.6 eV). In general samples were ground to a particle size of $\sim 50\ \mu$m and pressed into a gold-plated mesh. For the oxide systems a thin layer of gold was deposited on the surface of each sample to compensate for charging effects[17]. Binding energies were measured relative to the gold $4f_{7/2}$ line taken at 84.0 eV. The values are listed in

TABLE. 2p Binding Energies, Spin-Orbit Separations and Peak Widths ($\Delta_{1/2}$) for Various Chromium Compounds.

Compound	Formal Chromium Oxidation State	2p Binding Energies (eV)[a]				
		$2p_{3/2}$	$\Delta_{1/2}$	$2p_{1/2}$	$\Delta_{1/2}$	$(2p_{1/2}-2p_{3/2})$
Li_2CrO_4	VI	579.8	(1.7)	589.0	(2.4)	9.2
Na_2CrO_4	VI	579.8	(2.0)	589.1	(2.6)	9.3
K_2CrO_4	VI	579.6	(1.8)	588.9	(2.3)	9.3
Cs_2CrO_4	VI	579.8	(2.1)	588.8		9.0
$CaCrO_4$	VI	578.9	(2.2)	588.1	(2.3)	9.2
$SrCrO_4$	VI	579.6	(2.2)	588.6	(2.1)	9.0
$BaCrO_4$	VI	579.1	(2.2)	588.4	(2.5)	9.3
$Na_2Cr_2O_7$	VI	579.4	(2.0)	588.5		9.1
$K_2Cr_2O_7$	VI	579.4	(2.3)	588.8		9.4
$Rb_2Cr_2O_7$	VI	579.4	(2.1)	588.7		9.3
$Cs_2Cr_2O_7$	VI	579.5	(2.3)	588.7	(2.7)	9.2
K_3CrF_6	III	583.0	(2.7)	593.2	(4.0)	10.2
$(NH_4)_3CrF_6$	III	579.5	(2.9)	589.7	(3.4)	10.2
$Cr(NH_3)_6Cl_3$	III	578.5	(3.1)	588.2	(3.4)	9.7
$Cr(en)_3Cl_3$	III	578.3	(3.1)	588.0	(3.0)	9.7
$LiCrO_2$	III	577.0	(3.0)	586.8	(3.1)	9.8
$NaCrO_2$	III	577.0	(2.8)	586.9	(3.4)	9.9
$CuCrO_2$	III	576.4	(3.3)	586.2	(3.5)	9.8
Cr_2O_3	III	576.8	(3.0)	586.5	(3.2)	9.7
$Cr(acac)_3$	III	577.7	(3.3)	587.4	(3.4)	9.7
$K_3[Cr(ox)_3]$	III	578.8	(3.4)	588.3	(4.7)	9.5
$Cr_2(CO_4)_3 \cdot xH_2O$	III	580.2	(3.4)	589.8	(3.8)	9.6
$KCr(SO_4)_2 \cdot 12H_2O$	III	581.0	(3.3)	590.5	(3.2)	9.5
$CrCl_3$	III	577.8	(2.9)	587.4	(2.9)	9.6
$[Cr(urea)_6]Cl_3$	III	579.9	(3.4)	589.3	(3.4)	9.4
$K_3[Cr(NCS)_6]$	III	577.7	(3.6)	586.9	(3.9)	9.2
$Cr(HFA)_3$[b]	III	580.6	(2.8)	589.6		9.0
$Cr(\pi-C_5H_5)_2$[b]	II	576.9	(2.5)	585.9		9.0
$Cr(CO)_6$[b]	0	578.5	(1.8)	587.5		9.0
$Cr(CO)_6$	0	577.6	(2.3)	586.3	(3.2)	8.7
$Cr(metal)$	0	573.8	(2.0)	583.0	(2.4)	9.2

[a] Relative to Au $4f_{7/2}$ at 84.0 eV. Oxide values taken from Ref. 17. en = ethylene diamine, acac = acetylacetonate, ox = oxalate, HFA = hexafluoroacetylacetonate. [b] Ref. 9.

the Table. For many of the chromium(III) complexes it was not possible to use the gold decoration technique due to induced decomposition at the surface. The values recorded for these compounds are referenced to the gold line recorded from the sample holder but little credence should be given to the absolute values of the $2p_{3/2}$, $2p_{1/2}$ binding energies since a certain amount of surface charging almost certainly occurred. However, despite this problem the value of the $2p_{3/2}$–$2p_{1/2}$ separation should be unaffected by errors in the absolute binding energies and it is these separations that are of present interest.

Results

The Table lists the compounds studied together with the binding energies of the $2p_{3/2}$ and $2p_{1/2}$ peaks,

their measured full width at half maximum peak height values ($\Delta_{1/2}$) and the spin–orbit separations. The compounds are grouped in order of decreasing formal oxidation state of the chromium atom. Generally speaking the Cr(VI) compounds, of electronic configuration $3d^0$, possessed sharper peak profiles and showed a smaller spin–orbit separation than the Cr(III) compounds in which the $3d^3$ configuration gives rise to a state with a total spin of 3/2. However, it may be seen that the Cr(III) complexes showed a wide variety of spin–orbit separations and the lower end of the range overlapped with the Cr(VI) values. The relative magnitude of the splitting for each complex followed the general trends of the nephelauxetic series[20], see further.

On the other hand, the $3d^6$ spin-paired Cr(0) complex $Cr(CO)_6$ showed a $2p_{3/2}$–$2p_{1/2}$ separation of 8.7 eV which was marginally less than that recorded

for the metal. Similar results have been obtained by Clarke and Adams[9] and by Pignataro, Foffani and Distefano[19] for various Cr(0) systems.

Discussion

The Nature of the 2p Peak Doublet

The characteristics of the $2p$ doublet are its energy, shape and separation. The energy at which the peak doublet appears is governed by the orbital charge density distribution (subject, of course to shifts attributable to surface charging effects) and will not be considered further. The shape and separation of the doublet, however, are modified by the unpaired orbital spin density distribution and it is the effect of covalency upon this spin density which is to be considered here.

Primarily, the magnitude of the peak doublet separation is governed by the degree of spin–orbit coupling within the atom (the spin–orbit coupling constant is $\xi_{n,1}$ where n and l are the principal and orbital angular momentum quantum numbers respectively). The spin–orbit interaction is essentially a function of atomic number[21], see below, and although reduced below its free-ion value by covalency effects in the case of valence orbitals[22] is not expected in the case of core orbitals to be largely affected by changes in chemical environment. It is important, however, to be sure that this is the case since in the situation where the $2p$ peak doublet has a multiplet structure, movements in the weighted centres of the multi-component peak doublet could be overshadowed by changes in the primary separation due to an alteration in the value of ξ_{2p}. If the initial state has non-zero angular momentum, J, then the hole created by photoejection of a $2p$ core electron can couple to J in more than one way to form several final states. This is termed *multiplet splitting*. In an initial spin zero state, with a non-spherically symmetric electrostatic environment, Coulombic and exchange effects can lead to *electrostatic splitting* of the core level following photoejection. The magnitude of these effects is small, $\cong 1$ eV for the $2p$ level, compared to ξ_{2p} which is of the order of 15 eV; it is for this reason important to be sure that ξ_{2p} is constant when considering the reasons for changes in the $2p_{3/2}$–$2p_{1/2}$ separation.

The $2p$ multiplet splitting is expected from calculations[2,3,23] to be much smaller than $3s$ splittings because of the smaller exchange interaction between $2p$ and $3d$ electrons. This fact coupled with the greater complexity of the final states in the $2p$ case means that *experimentally* each of the spin–orbit levels will be broadened by up to 2 eV for complexes with unpaired d electrons; the observation of the multiplet components must await an improvement in the resolving power of the technique through a reduction in the bandwidth of the exciting radiation.

Nefedov[13], assuming jj coupling in the $2p$ shell and considering the electrostatic interaction of the $2p$, $3d$ electrons as a perturbation, calculated splittings of the $2p_{1/2}$ and $2p_{3/2}$ levels into their components and showed how changes in the doublet separation could be explained by a movement of the weighted centre of the multiplets which depended upon the magnitude of the exchange interaction G ($2p$, $3d$). These calculations assumed a valence electron state of the same multiplicity as the ground state on the argument that the orbital angular momentum of the $3d$ electrons is quenched by the ligand field. The behaviour of these levels calculated using the secular matrices of Nefedov for the $3d^3$ configuration is illustrated in the Figure. As can be seen, the weighted centre of the multiplets comprising the $2p_{3/2}$ and $2p_{1/2}$ peaks move apart as the exchange interaction increases. This rather simplified approach thus qualitatively indicates that an increase in exchange interaction should result in a broadening of the doublet components and an increase in their separation.

The Effect of Covalency on the Spin–Orbit Coupling Constant

Bonding in transition metal compounds can be described in terms of the nephelauxetic effect which may be understood as a measure of covalency and related to the stability of particular oxidation states. It is conceptually convenient to recognise two covalent contributions operating within the nephelauxetic effect[20], central field covalency, due to a reduction of the effective positive charge on the metal by the screening of the d^n configuration by the ligands, and
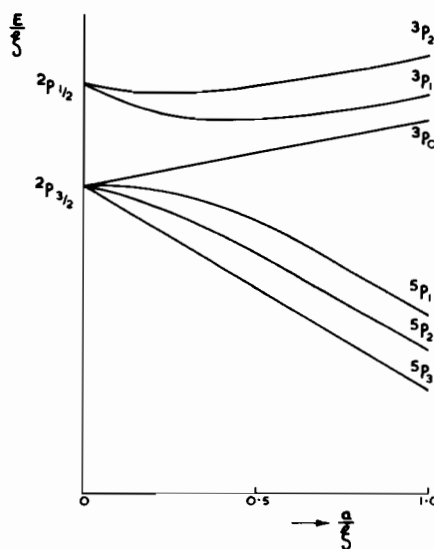
Splitting of the $2p$ levels by $3d$ electrons in Cr^{3+} ($s = 3/2$). ξ = spin orbit coupling constant, $\alpha = 2p3d$ exchange integral.

symmetry restricted covalency due to participation of the metal d orbitals in molecular orbital formation with the ligand orbitals. It is difficult to assess from nephelauxetic parameters alone the magnitude of the two contributions but it appears that a consideration of the degree to which the $2p_{3/2}-2p_{1/2}$ separation is altered by changes in oxidation state can aid this assessment; this is considered below in the following section.

Little is known at present about the variation of spin–orbit coupling constants as a function of central ion and ligands but this has been investigated in a recent publication[22] in which $\xi_{n,l}$ (r) was calculated for a range of oxidation states of metal ions in the $3d$ series. The value of ξ may be represented as follows:

$$\xi = \frac{1}{2}\alpha^2\{Z\int_0^\infty r^{-3}R^2(r)r^2dr-$$
$$\Sigma_i\int_0^\infty r^{-3}R^2(r)r^2dr\int_0^r R^2(r_i)r_i^2dr_i\} \quad (1)$$

where only the nuclear attraction and direct screening terms are included. It may be seen that ξ is primarily a function of Z (atomic number) and r^{-3}, where r is the distance from the nucleus in a.u. Since ξ is proportional to $<r^{-3}>$ it is predominantly an inner radial function and calculations showed that the major part of the total value of $\xi_{n,l}$ originates from interactions in the region between 0.2 and 0.8 a.u., so that for the CrF_6^{3-} ion, for example, ξ_{3d} reaches virtually its infinity value at distances from the metal much smaller than those at which significant metal–ligand overlap takes place. Consequently it is to be expected that central field covalency will make only a minor contribution to the reduction of ξ_{3d} accompanying complex formation, and it has thus been concluded[22] that symmetry restricted covalency plays the major role in the reduction of ξ_{3d} below the free ion value.

Correlation with Observed Spectra

The values for the spin–orbit separations listed in the Table show two trends. Firstly, the value for the chromium(0) cases (9.1 eV average) is very similar to that for chromium(VI) cases (9.2 eV average), and secondly, the chromium(III) complexes show a marked variation in this parameter. As mentioned above, the value of the spin–orbit coupling constant $\xi_{n,l}$ will depend upon the atomic number Z and the electronic screening terms in equation (1). From the data in the Table it may thus be concluded that, since very little alteration in the value of the $2p_{3/2}-2p_{1/2}$ separation is engendered by a change of six in the formal oxidation state, the effect of removing six d electrons is hardly noticeable as far as the screening of the $2p$ orbital is concerned. It is unlikely that electrostatic effects will alter the peak separations since the metal valence electronic distribution may be considered to be spherically symmetric in the d^0, d^3 and d^6 situations. It therefore seems fair to conclude that ξ_{2p} is

essentially unchanged and that the variations in the $2p_{3/2}-2p_{1/2}$ separation for the d^3 complexes must be due to a variation in the degree of spin delocalisation in the valence orbitals which alters the exchange interaction G(2p, 3d). An increase in the separation of the doublet and broadening of the individual peaks is predicted by Nefedov's theory, as described above, for compounds with unpaired electrons, and it can be seen from the data in the Table that these trends are observed in general for the d^3 series. It is interesting to note, however, that in compounds in which the low β values derived from electronic absorption spectra indicate that the chromium/ligand bond is covalent, e.g. $K_3[Cr(NCS)_6]$,[24] the doublet separation is the same as that in complexes where there are no unpaired electrons, whereas in the more ionic complexes, e.g. K_3CrF_6, the separation is ca. 1 eV greater. This ordering of the spin–orbit splitting thus follows the nephelauxetic series[20] and gives a clear indication that in the more covalent compounds the spin delocalisation is substantially complete, i.e. that in these compounds the metal d orbitals are sufficiently expanded to preclude measurable interaction with the $2p$ core electrons. Similarly in the d^2 compound $Cr(\pi-C_5H_5)_2$ the spin–orbit splitting indicates a high degree of spin delocalisation. Carver et al.[4] in their study of $3s$ multiplet splittings found that alterations in the degree of splitting followed the nephelauxetic series for chromium and manganese compounds, but the $3s$ situation is unhampered by spin–orbit effects.

The observation that ξ_{2p} remains essentially constant whilst wide variations in effective nuclear charge and covalency occur substantiate the conclusion[22] that central field effects are small and symmetry restricted covalency is dominant. Clearly the screening effect of ligands is negligible at the $2p$ level. It would be of interest to observe changes in the multiplet structure of $3p$ peaks to ascertain whether screening was occurring at this level; from such data it would be possible to deduce the degree of ligand orbital penetration into the central ion. Unfortunately the resolution of our present spectrometer precludes such a study.

Acknowledgement

References

1 H. Basch, *Chem. Phys. Letters*, 20, 233 (1973).
2 C.S. Fadley, D.A. Shirley, A.J. Freeman, P.S. Bagus and J.V. Mallow, *Phys. Rev. Letters*, 23, 1397 (1969).
3 C.S. Fadley and D.A. Shirley, *Phys. Rev.*, A2, 1109 (1970).

4 J.C. Carver, G.K. Schweitzer and T.A. Carlson, *J. Chem. Phys., 57*, 973 (1972).
5 D.C. Frost, C.A. McDowell and I.S. Woolsey, *Chem. Phys. Letters, 17*, 320 (1972).
6 M.V. Zeller and R.G. Hayes, *Chem. Phys. Letters, 10*, 610 (1971).
7 A. Rosencwaig, G.K. Wertheim and G.J. Guggenheim, *Phys. Rev. Letters, 27*, 479 (1971).
8 G.K. Wertheim and A. Rosencwaig, *J. Chem. Phys., 54*, 3235 (1971).
9 D.T. Clark and D.B. Adams, *Chem. Phys. Letters, 10*, 121 (1971).
10 L.J. Matienzo, L.I. Yin, S.O. Grim and W.E. Swartz, *Inorg. Chem., 12*, 2762 (1973).
11 D. Briggs and V.A. Gibson, *Chem. Phys. Letters, 25*, 493 (1974).
12 A.J. Freeman and D.E. Ellis, *Phys. Rev. Letters, 24*, 516 (1970).
13 V.I. Nefedov, *Bull. Acad. Sci. USSR, Phys. Ser., 28*, 724 (1964).

14 D.N. Hendrickson, J.M. Hollander and W.L. Jolly, *Inorg. Chem., 9*, 162 (1970).
15 R. Prins and T. Novakov, *Chem. Phys. Letters, 16*, 86 (1972).
16 J.A. Connor, I.H. Hillier, V.R. Saunders, M.H. Wood and M. Barber, *Mol. Phys., 24*, 497 (1972).
17 G.C. Allen, M.T. Curtis, A.J. Hooper and P.M. Tucker, *J. Chem. Soc. Dalton*, 1675 (1973).
18 J.C. Helmer, *J. Electron Spectrosc., 1*, 259 (1972).
19 S. Pignataro, A. Foffani and G. Distefano, *Chem. Phys. Letters, 20*, 350 (1973).
20 C.K. Jorgensen, "Progress in Inorganic Chemistry", *4*, 73 (1962).
21 U. Gelius, *Physica Scripta, 9*, 133 (1974).
22 R. Al-Mobarak and K.D. Warren, *Chem. Phys. Letters, 21*, 513 (1973).
23 C.S. Fadley and D.A. Shirley, *Phys. Rev. Letters, 21*, 980 (1968).
24 C.K. Jorgensen, "Oxidation Numbers and Oxidation States", Springer-Verlag, 1969, Chapter 5.